

THE DETECTION AND MEASUREMENT OF HYDROGEN SULPHIDE

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A thesis submitted to the University of Nottingham
for the degree of Doctor of Philosophy
in the School of Life and Environmental Sciences

December 2002

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ACKNOWLEDGEMENTS

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ACKNOWLEDGMENTS

Firstly, I would like to acknowledge my considerable debt to Dr Jeremy J Colls for his guidance and supervision throughout the many years since I initially approached him with my suggestion for this project. I don't think either of us anticipated that this work would expand in the way it has.

Additionally, I would like to thank Dr Jerry A Clark, for his encouragement and supervision during the first part of this work, and Dr Scott D Young for his supervision and assistance during the latter part. I am particularly grateful to all three of my supervisors for coping with my eccentricities and idiosyncrasies in such a constructive manner.

I would also like to thank all those who have given any technical, administrative or educational help during the course of my research. There are just too many to name individually, but I would like to express my thanks to everyone who as helped in any way. This includes the assistance of numerous commercial bodies, and their representatives, who have loaned equipment and given freely of their time and expertise.

Finally, I gratefully record the parts played by my wife, Jan, and our sons Jacob and Joseph, without whose help, support and encouragement I might never have begun this.

ABSTRACT

Gas measurement techniques for hydrogen sulphide (H_2S) have been investigated, with particular reference to the monitoring of average ambient concentrations and also the rapidly changing concentrations which may be associated with vehicle pollution. Two new techniques have been identified, and new equipment built and tested, for H_2S determination. The first of these is designed to measure long term average concentrations of H_2S and the second to evaluate rapidly changing peak concentrations over very short periods of time.

The implementation of catalytic converters in modern petrol driven motor vehicles has resulted in undesirable emissions of hydrogen sulphide gas. The reasons for these emissions are discussed. Ambient concentrations of H_2S have been measured at the roadside and the average contribution originating from vehicular emissions on major roads determined. Results are presented which confirm the elevation of hydrogen sulphide concentrations at the road side of an average of single figure parts per billion. Peak H_2S concentrations of up to 100 ppb were also measured at the roadside and within motor vehicles. The peaks were of very short duration and therefore of only minimal contribution to average ambient concentrations.

Measurements of H_2S concentrations at a variety of locations have also been made, and results are presented, of comparisons between areas with no source of H_2S nearby, roadside sites and other possible H_2S sources such as sewage treatment works and landfill sites.

Known H_2S concentrations, in excess of 500 ppm from a point source on a landfill site, were found to diminish rapidly toward zero, within 150 m of the source. This demonstrated the high reactivity of H_2S and therefore the importance of measuring H_2S concentration as closely as possible to the emission source. Consequently, this high reactivity is particularly important in the consideration of roadside and 'on-road' monitoring of H_2S .

A NOTE ON UNITS AND CONVENTIONS

For consistency, units quoted throughout use the *Système Internationale d'Unités* (SI). In many instances, quantities shown have been converted from other units to a close approximation.

Symbols in circuit diagrams follow conventional publishing practice - which differs in some respects from the appropriate British Standards.

Component values in circuit diagrams are shown using 'unit point' practice which avoids possible ambiguities in the meaning of the decimal point. For example $1\text{M}2 = 1.2\text{ M}\Omega$, $220\text{k} = 220\text{ k}\Omega$, $100\text{R} = 100\ \Omega$ and $0\text{F}1 = 0.1\text{ FF}$.

“Until recently it was commonly assumed that the air, water and earth had miraculous powers of regeneration and recuperation. Each community was an open system through which flowed streams of clean air and water, sweeping away pollutants that were subsequently rendered harmless by natural processes. We have come to see the inadequacies of this view...” (Fay, 1971)

Chapter 1: INTRODUCTION

1.1 BACKGROUND

1.1.1 Air pollution and vehicles

The subject of air pollution became of increasing concern in the second half of the twentieth century. Motor vehicle pollution was one aspect which received particular attention, because despite the increasing use of motor vehicles, opportunities were seen for a reduction in the pollution produced. These included changing the constituents of the fuel used, improving the efficiency of its combustion, the introduction of catalytic converters and changing vehicle designs and components to produce lighter vehicles which use less fuel, and therefore produce less pollution, per mile travelled. For example, recent advances in the development of ultra-light steel for vehicle suspension systems have resulted in weight savings of up to 34% compared with conventional steel (Anon., 2001).

Motor vehicles have become an indispensable part of modern society but the pollution they produce is exhausted into the same micro environment as that in which most people lead their everyday lives. Those most at risk from any adverse effects are the road users themselves - both those in vehicles (Clifford *et al.*, 1997) and those exercising or walking by the roadside (Natusch and Slatt, 1978; Quality of Urban Air Review Group (QUARG), 1993). Therefore motor vehicle pollution contrasts with the majority of industrial pollution which can travel large distances - allowing mixing, dilution and other mechanisms to reduce the eventual effects on the environment.

The main chemical constituents of motor vehicle pollution are well documented. Carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC) are regulated in some regions by law (Federal Register, 1986; cited in Westerholm *et al.*, 1996), and are the constituents which three-way catalytic converters were

designed to reduce, but there are also a large number of unregulated constituents which contribute to air pollution in varying amounts, depending on the fuel used as well as the type of engine and how well it is maintained.

Hydrogen sulphide is one such constituent and, in their 'Recommendations for Further Research', the Department of Health Advisory Group on the Medical Aspects of Air Pollution Episodes (1992), advocated much more research into the effects of airborne pollutants in general terms, and sulphur compounds in particular.

However, hydrogen sulphide in the atmosphere has many origins other than motor vehicles. Worldwide, the greatest proportion is from natural sources - such as volcanic activity and the anaerobic decomposition of organic matter - but humankind also contributes with emissions from industrial processes, sewers and animal wastes. Strauss and Mainwaring (1984) quoted the following figures¹ (Table 1.1) for the quantities of sulphur dioxide and hydrogen sulphide emitted from natural and man made sources.

Table 1.1. Emissions of SO₂ and H₂S for anthropogenic and natural sources.

Gas	Man Made (Tg yr ⁻¹)	Natural (Tg yr ⁻¹)
Sulphur dioxide	148	6-12
Hydrogen sulphide	3	30-102

Shooter (1999) suggested that H₂S played a decreasing role in the sulphur budget but Watts (2000) maintained that there was much greater uncertainty.

1

These figures were originally quoted in Imperial tons and have been nominally converted to Système Internationale (SI) units. All subsequent data has been similarly treated.

Although SO₂ emissions have declined during the 1980s and 90s, as seen in Figure 1.1, the majority of sulphur-based compounds emitted to the atmosphere (ie. all forms included), are still anthropogenic (~160 TgS yr⁻¹) rather than natural (~50 TgS yr⁻¹) and do not appear to be decreasing (Bates *et al.*, 1992). The dominant anthropogenic source is still SO₂ from fossil fuel burning and the dominant natural sources are carbonyl sulphide (OCS) and dimethyl sulphide (DMS).

On a world scale, therefore, hydrogen sulphide from vehicle pollution might seem to be a minor problem, but the present concern is that such emissions might have a detrimental effect on crops, people and animals close to the point of emission, particularly drivers of other vehicles, pedestrians and cyclists (Deuchar *et al.*, 1999).

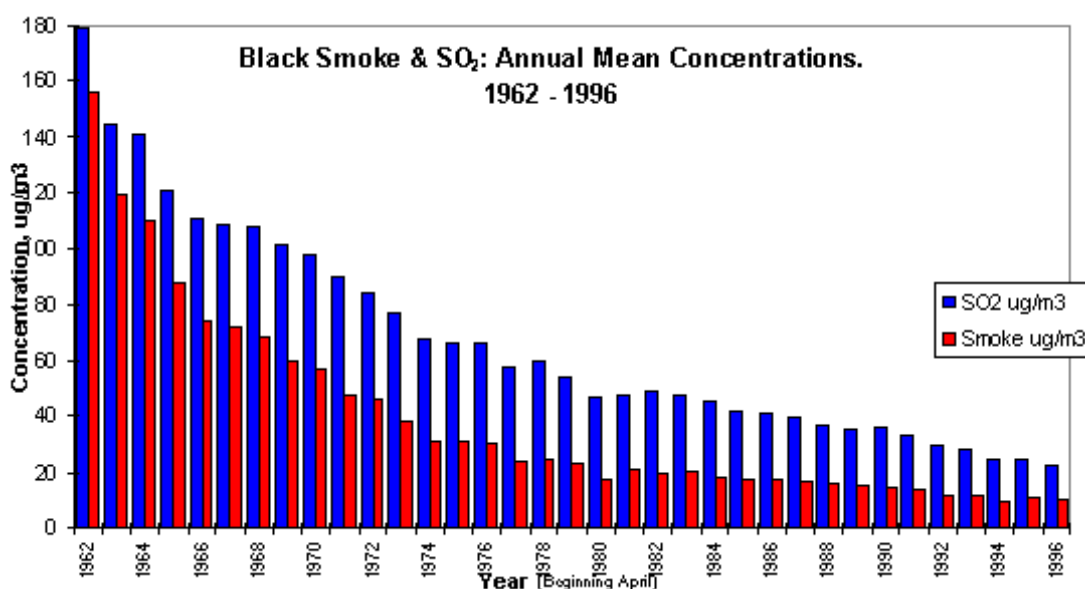


Figure 1.1 Mean annual concentrations of black smoke and SO₂ in the UK (UK National Air Quality Information Archive at <http://www.aeat.co.uk/netcen/airqual/home.html>)

1.1.2 Hydrogen sulphide (H₂S) emissions from vehicles

The first observation of H₂S in vehicle exhaust gases is believed to have been made in 1974 by Chrysler technicians testing early catalytic converters (U.S.Environmental Protection Agency, 1974). The effect was generally considered a minor byproduct of catalytic action, due to the chemical reduction of sulphur dioxide, and not investigated further. However, the first report of the Quality of Urban Air Review Group (1993), remarked that “Catalytic converters can be associated with emissions of hydrogen sulphide, which may constitute a local nuisance rather than a health issue”. In the context of the compulsory introduction of catalytic converters in the United Kingdom (effective for new vehicles from 1st January 1993) this was a reasonable view. Other contemporary studies (Wehinger and MeyerPittroff, 1994; eg. Westerholm *et al.*, 1996) were also unconcerned about H₂S emissions.

The potential for H₂S emissions from vehicles exists simply because sulphur exists in petroleum. From the combustion chamber, sulphur, in elemental or compound form, will pass to the catalytic converter. Here, carbon monoxide and hydrocarbons will be oxidised to carbon dioxide and water whilst, at the same time, nitrogen oxides will be reduced to nitrogen and oxygen. Superficially, these contradictory requirements appear possible through the transfer of oxygen from one compound to another, but in practice a fine balance of temperature and mixture control is required (U.S.Environmental Protection Agency, 1974; Simpson, 1975; Watkins, 1991). The situation is further complicated by differing driving conditions and differing mixture requirements depending on whether the vehicle is accelerating, running at constant speed or decelerating (Seinfeld, 1986). Engine loadings, whether due to varying payload or gradients, will obviously have similar effects.

In the converter numerous different reactions take place - many of which are non-preferred - as compromises are made in catalytic converter construction with the

aim of producing an acceptable exhaust composition. The interior of a typical catalytic converter is seen in Figure 1.2.

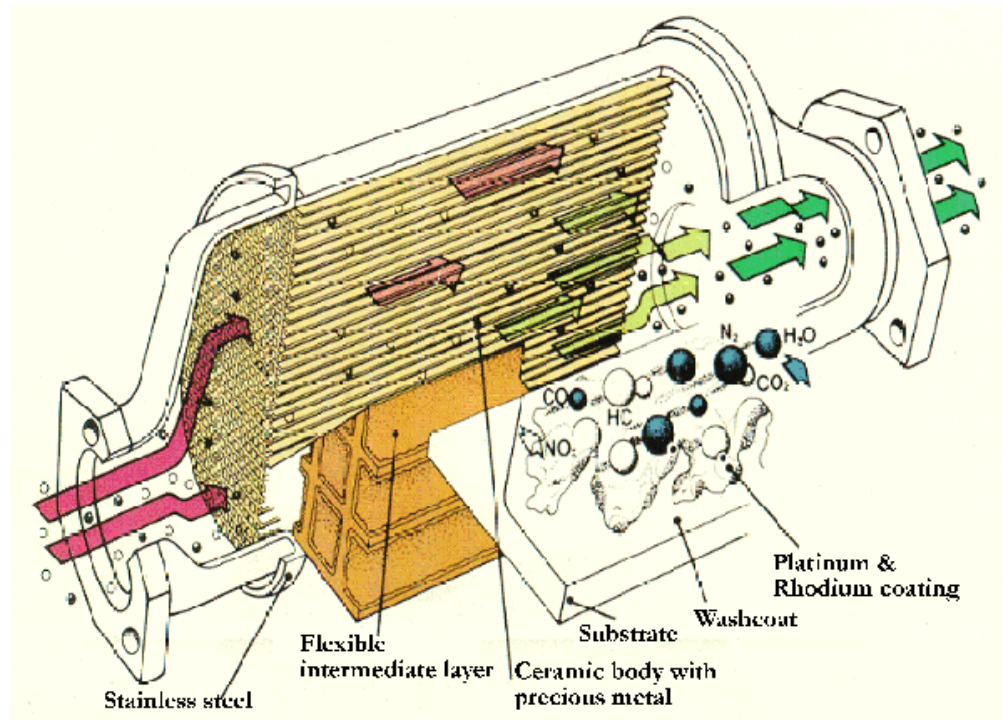


Figure 1.2 Cross section through three way catalytic converter (courtesy Audi Motors)

For example, nickel is sometimes a constituent of engine system components and has been used in catalytic converters. It has an affinity for sulphur, which it will remove (Thomas, 1970). Thereby it will protect other sulphur sensitive catalysts and the nickel catalyst is discarded after becoming sulphided. Although employed in the United States, the European Community views this discarding of nickel as undesirable and forbids its use. A further reason for not using nickel is that it acts as a catalyst in an undesirable reaction which leads to the production of methane (Gates, 1996) - a gas known to increase global warming. Figure 1.3 shows sulphur deposits around the tail pipes of early catalytic vehicles.



'J' registration (1993) Ford



'J' registration (1993) Volvo

Figure 1.3 Visible sulphur deposits around the tail pipes of vehicles fitted with catalytic converters.

In addition to the catalytic converter's components and exhaust gas constituents, there are potential contaminants from other sources such as phosphorous, lead, zinc, calcium, magnesium and barium from engine oils or fuels, and iron, copper, nickel and chrome from engine system components (McArthur, 1975). These make the possibilities for unpredictable reactions almost limitless. Twenty three "important" sulphur reactions in three-way catalysts are listed by Seinfeld (1986).

Around thirteen base and noble metals have been used in catalytic converters. All of these are each capable of being sulphided at one particular temperature and can theoretically release sulphur, in the form of hydrogen sulphide, at a second, higher temperature. Both ranges of temperatures are within the normal working range of the converter (Simpson, 1975). The same study showed that for a (then typical, see section 1.1.3) sulphur content of 300 ppm in the fuel, the theoretical concentration of H_2S in the exhaust gas could be as much as 20 ppm by volume.

Engine maintenance is a factor in the effectiveness of any catalytic converter. It has been shown (Seinfeld, 1986; Watkins, 1991) that deviation from the stoichiometric air:fuel ratio of 14.7 by as little as one per cent, toward a leaner mixture, can reduce the NO_x conversion efficiency by up to 10 %. Although lean mixtures have only minor effects on HC and CO, similar one per cent changes toward a richer

mixture can reduce the efficiency of catalysis by some 20 % and 40 % respectively.

Cadle and Mulawa (1978) and Fried, Henry, Ragazzi, *et al.*, (1992) investigated a number of vehicles and concluded that rich mixtures, in conjunction with high catalytic converter temperatures, can lead to reducing conditions in which H₂S can also be produced. More recently, Watts (1999) concluded that roadside H₂S concentrations were elevated as a result of the introduction of catalytic converters.

It is generally acknowledged that toward the end of the lifespan of any vehicle, as its value declines, that there is a tendency for later owners to resort to inappropriate maintenance. This was confirmed in the US (Calvert *et al.*, 1993) where, after several years of catalytic converter use, higher emission rates than expected occurred in 20 % of cars investigated. The prime reason was the use of more acceleration than expected, but the second and third reasons, were tampering and mis-fuelling respectively - where one tank of leaded fuel can cause major poisoning of the catalyst. Such factors need to be taken into account in estimates of future global pollution.

1.1.3 Road users perceptions

Hydrogen sulphide has been a difficult gas to quantify and, as will be discussed later, only recent advances in instrumentation have made accurate measurement at low concentrations possible with portable instruments. Although the 'rotten eggs' smell of H₂S is easily recognised, and universally disliked (Moncrieff, 1966), the threshold of detection by the human nose is inconsistent. The fact that hydrogen sulphide in vehicle emissions was originally detected by smell, suggests that the nose is a suitable guide to its concentration. Unfortunately, the situation is not so straightforward, as perceptions of H₂S odour vary enormously from one individual to another.

Five ppm is often quoted as the lower limit of detection by the human nose (eg Lenga, 1988) but this figure varies from one person to another. Warner (1976) quoted a number of studies conducted between 1939 and 1968 which showed that the odour threshold for hydrogen sulphide varied from 0.0065 - 0.7 ppm. It was Warner's belief that the actual odour threshold is 0.00047 ppm, but that water vapour and impurities raise this level and so 0.0047 ppm is a more realistic figure, still three orders of magnitude below 5 ppm. A more recent worker (Smith, 1983) also asserted that the actual odour threshold is 0.0005 ppm thereby supporting Warner's figure.

Hence, there is a problem in subjective measurement of hydrogen sulphide concentrations, probably due to rapid olfactory fatigue as the concentration increases. Warner suggested that hydrogen sulphide odour is "distinct" at 0.35 ppm, "offensive and moderately intense" at 2.8 - 5.6 ppm and "strong but not intolerable" at 21 - 35 ppm, but not as intense at 226 ppm due to paralysis of the olfactory nerves. He went on to advise that the maximum urban concentration of hydrogen sulphide should lie between 0.001 to 0.009 ppm and thereby implied that as little as 1 ppb is potentially harmful. Therefore, to encompass Warner's recommendation and Lenga's viewpoint, the range initially considered in the current work was between 1 ppb and 5 ppm hydrogen sulphide by volume.

It seems likely, as with other odours, that even at very low levels that there is some olfactory desensitisation within a few seconds of the first exposure. However hydrogen sulphide is unusual in that this is a physiological response rather than solely psychological filtering (Beauchamp, Jr. *et al.*, 1984; World Health Organization, 1996). This effect could account for the wide range of threshold measurements reported. As will be discussed later in the section on reactivity (1.2.3), the lifespan of H₂S in ambient air is short. When combined with the relatively brief emissions of H₂S from vehicles fitted with catalytic converters reported by Cadle and Mulawa (1978), these factors confirm anecdotal evidence from road users that H₂S emissions are fleeting, but pungent, and so make it harder

to evaluate subjective measurements.

In Australia, the first catalyst-equipped cars appeared in 1985 and numerous complaints of unpleasant odours soon followed. After a literature review and a preliminary study of the chemistry occurring in the catalyst, a further study (Williams *et al.*, 1987) was published under restriction. This important work included extensive on-line testing of a variety of vehicles under varying conditions and with varying sulphur content in the fuel. Williams *et al.* decided that three factors were involved in odour emission - the presence of a catalyst, the sulphur content of the petrol and reducing conditions in the exhaust. They concluded that reduction of the sulphur content of fuel was the only feasible method of control.

In 1993 it was estimated that it would take 15 years, from commencement in 1990, for existing vehicle fleets to be replaced by catalyst-equipped vehicles throughout Europe (Arco Chemical Europe Inc, 1993). Also, in the absence of fuel reformulation, it would be some 10 years before the older, more polluting, cars were responsible for less than 50 % of total exhaust emissions. An increasing proportion of diesel-engined vehicles would tend to reduce this percentage, although such growth might be tempered by the assertion that diesel pollution could have health costs up to two and a half times higher than those of petrol engined vehicles (Eyre *et al.*, 1995).

In fact, there have been considerable developments in fuel technology in the 1990s with far reaching implications for the subject matter of this project. Watkins (1991) noted that there were no emission standards, for vehicles, for any sulphur products, but there were air quality standards for sulphur dioxide within the European Community. Both leaded and unleaded petrol could then contain 0.2% (by weight) of sulphur and diesel fuel could contain a similar proportion (Watkins, 1991) At that time European petrol contained a maximum of 240 ppm (by weight) of sulphur compared to 340 ppm in US 'gasoline'.

In 2000, UK petrol companies were already reducing the sulphur content of fuels in anticipation of forthcoming mandatory reductions. Figures for January 2001 of the sulphur content of fuels for Texaco UK and BP Oil UK are given in Table 1.2 below, along with the mandatory levels then current in the European Community (EN590), and anticipated (Branif, S, 2001, personal communication and Newey, J, 2001, personal communication).

Table 1.2. Sulphur content of fuels

	LRP	SU	ULSU	SD	ULSD
Texaco 2000	124	124	45	400	40
BP 2000	120	120	50	280	43
Mandatory 2001	150	150	150	350	350
Mandatory 2005	N/A	N/A	50	N/A	50

All figures in ppm (w/w), LRP= lead replacement petrol, SU= standard/premium/super unleaded, ULSU= ultra low sulphur unleaded, SD= standard/regular diesel, ULSD= ultra low sulphur diesel.

These are very considerable reductions and should do much to reduce all forms of sulphur based pollution originating from vehicles - especially if considered in tandem with continually improving vehicle fuel economy.

1.2 HYDROGEN SULPHIDE (H₂S) PROPERTIES

1.2.1 Chemical and physical properties

Hydrogen sulphide is a colourless gas with an offensive odour and is highly flammable, in both liquid and gaseous forms. It may produce explosive mixtures with air (Lenga, 1988) and may ignite on contact with a wide range of metal oxides (Royal Society of Chemistry, 1981).

The structure of hydrogen sulphide is analogous to that of water. H_2S is also highly soluble in water (2.6 L of gas dissolve in 1 L of water at 20 °C), forming a slightly acidic solution which may be oxidised by atmospheric oxygen to give a milky sulphur precipitate. (Pauling and Pauling, 1975).

Reactions between H_2S and oxygen are particularly important in this study and are discussed in more detail in section 1.2.2. H_2S gas will readily attack copper and blacken silver but aluminium and carbon steel are fairly resistant. On the other hand, H_2S dissolved in water can corrode steel at a rate of up to 2.5 mm per year (Beauchamp, Jr. *et al.*, 1984).

The physical properties of hydrogen sulphide are shown in Table 1.3.

Table 1.3. Physical properties of H_2S

1mg.m^{-3}	0.670 ppm H_2S in air
Melting point	-85.5 °C
Boiling point	-60.7 °C
Density	1.54 g/L @ 0 °C
Water solubility	4370 mL/L @ 0 °C, 1860 mL/L @ 40 °C
Vapour pressure	1875 kPa @ 20 °C

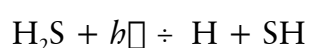
(World Health Organization, 1996)

1.2.2 Reactivity

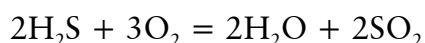
Within two to forty eight hours of emission, hydrogen sulphide reacts with atmospheric ozone to produce sulphur dioxide, and is therefore an indirect source of SO_2 (Strauss and Mainwaring, 1984). Other reactions also contribute to the oxidation of H_2S to SO_2 , but Strauss and Mainwaring (1984) confirmed that all hydrogen sulphide is ultimately converted to sulphur dioxide in the atmosphere. Taking into account the different molecular masses, they argue that the total

sulphur dioxide and hydrogen sulphide emissions from natural sources are similar to those from pollutant sources. This finding was supported by Bates *et al.* (1992).

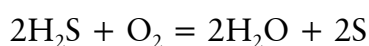
Hydrogen sulphide can be dissociated by photolysis by ultra-violet light in the wavelength range 180 - 270 nm (Andersson *et al.*, 1974; Wilson *et al.*, 1996). This is rare in the troposphere but diurnal fluctuations have been observed near H₂S sources and photolysis may be a factor (Tarver and Dasgupta, 1997). The reaction is of the form:



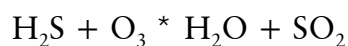
Under differing oxidising conditions H₂S may react to produce either SO₂ or S, along with water. If there is sufficient oxygen, S is fully oxidised to SO₂ (Beauchamp, Jr. *et al.*, 1984):



However, if oxygen is limited, the H₂S is converted to elemental sulphur:



Tropospheric ozone is also an effective oxidant:



The time for this oxidation to take place is discussed by Andersson *et al.* (1974). Cadle and Ledford (1966) suggest the lifespan of hydrogen sulphide in atmospheric ozone concentrations of 50 Fg m⁻³ is 1.7 days. By contrast Robinson and Robbins (1970) suggested a lifetime of two hours for H₂S in an urban atmosphere but regarded two days as appropriate for unpolluted air. An ozone concentration of 50 Fg m⁻³ approximates to 23 ppb, which is near the lower end of the 20-80 ppb

concentration range of ozone quoted for the clean troposphere (Seinfeld, 1986).

Hence, hydrogen sulphide from motor vehicle emissions is likely to remain present for periods of between two and forty eight hours - long enough to contribute to the exposure of people, and other life forms, to this form of air pollution.

1.2.3 Toxicology

Hydrogen sulphide is very toxic by inhalation, but is also of widespread occurrence (Health & Safety Executive and Factory Inspectorate, 1976). Like carbon monoxide and the cyanides it is also classed as an asphyxiant (U.S. Department of Health, 1994). H_2S is a respiratory inhibitor, that is it affects the part of the brain which controls the lungs, and is similar in action, and toxicity, to hydrogen cyanide. Riffat (1999) drew attention to the need for appropriate monitoring to warn workers of the presence of H_2S because of the olfactory paralysis that occurs. Deaths due to H_2S poisoning are often attributed to workers not being aware of the danger to which they were exposed (Fuller and Suruda, 2000).

Typical physiological responses to low concentrations of hydrogen sulphide (say, 1-20 ppm) are a sore throat, cough, shortness of breath, headaches, dizziness and conjunctivitis (Royal Society of Chemistry, 1981; Croner, 1990). Chronic H_2S poisoning has also been linked to spontaneous abortions in women at concentrations as low as 4 Fg m^{-3} (3 ppb) (Hemminki and Niemi, 1982; Xu *et al.*, 1998; Fielder *et al.*, 2000). Plants have also been shown to be highly sensitive to hydrogen sulphide emissions (Maas, 1987).

However, H_2S is highly reactive and combines rapidly with other elements to form less toxic compounds such as sulphur dioxide. The close relationships between H_2S , O_2 and SO_2 are important in this study and therefore neither of these sulphur species can be considered in isolation in terms of their effects. Sulphur dioxide is

a respiratory sensitiser which can aggravate other conditions as well as causing medical problems in its own right. Concentrations of SO₂ are currently decreasing in the atmosphere, accounting for less than 1 % of the total UK emissions (Williams, 1986; cited in Watkins, 1991). Nevertheless, in 1987, 50 % of roadside sulphur dioxide concentrations were derived from vehicular emissions (Bennet, 1987; cited in Watkins, 1991).

Hydrogen sulphide's characteristically unpleasant odour, of rotten eggs, serves both as a warning of its poisonous nature and as a repellant to those at risk. Unfortunately at high, and potentially lethal, concentrations this warning is lost due to olfactory paralysis (Warner, 1976; Beauchamp, Jr. *et al.*, 1984; Lenga, 1988). Consequently, health and safety concerns have led to increased monitoring for H₂S in the work place, where dangerous concentrations may be found (Anon., 1994). Commercial detection instruments, for safety monitoring, typically operate in the range 0-50 ppm but, below 5 ppm, manufacturers' data suggests the results are not very accurate (Section 2.2 gives details of proprietary instrumentation which has been assessed as part of this study). The figure of 5 ppm falls below recommended occupational exposure limits (OELs) (NIOSH, 1980; Royal Society of Chemistry, 1981; eg. Lenga, 1988) so accuracy below this concentration is not considered important in this kind of device. As discussed in section 1.1.3, the figure of 5 ppm is often quoted as the lower limit of detection by the human nose (eg. Lenga, 1988), but huge variations are observed between individuals.

In an extensive study of the toxicity of hydrogen sulphide (Beauchamp, Jr. *et al.*, 1984), it was noted that there was some disagreement over the manifestation of chronic intoxication due to the difficulties in objectively recording "the psychosomatic subjective nature of the signs and symptoms". The authors recommended a study to determine the effects on the respiratory, cardiovascular and central nervous systems and the eye. The same study also reported that carbon monoxide (CO) enhanced the toxic effects of H₂S. This has an obvious relevance in the context of vehicle emissions. Notwithstanding its highly toxic nature, no

evidence of teratogenicity, carcinogenicity or direct mutagenicity has been reported (Beauchamp, Jr. *et al.*, 1984; World Health Organization, 1996).

In Finland, 'The South Karelia Air Pollution Study' (Jaakkola *et al.*, 1990), looking at an anthropogenic source of H₂S emanating from the paper pulping industry, concluded that adverse human health effects occurred at long term concentrations as low as 10 ppb. Similar conclusions have been reached elsewhere (Bassmadzieva *et al.*, 1987). Although Warner (1976) suggested that concentrations should be kept below this value, he did not present evidence to support this assertion. Little is known about the chronic effects of low level H₂S exposure on humans, animals or plants. Most studies have been the result of localised industrial accidents (Arnold *et al.*, 1985; eg. Tvedt *et al.*, 1991; Kilburn, 1995; Hirsch and Zavala, 1999) but downward extrapolation from such data is not necessarily valid.

There appears to have been no specific research into the effects of slightly elevated concentrations of H₂S, with sporadic brief peaks of greater concentrations, as may occur with vehicle emissions. The nearest equivalent study compared an occupational, cross-sectional group of non-smoking sewerage workers with a similar group of water treatment workers (Richardson, 1995). This study concluded that the influence of hydrogen sulphide reduced lung 'forced expiratory volume' (FEV) by as much as 10 %.

The adverse health effects, reported in the Finnish study at concentrations of less than 10 ppb, seem to appear at very low concentrations when compared with typical international exposure limits of 10 - 20 ppm. This suggests that a re-think of occupational exposure levels is required. The relevance of exposure levels to the present work is that it seems likely that vehicle drivers will be subjected to much higher concentrations of H₂S than have so far been measured at the roadside and it needs to be ensured that at least the average concentrations fall below any revised OEL. Higher concentrations, and higher doses, of other pollutants (eg CO, ozone (O₃) and nitric oxide (NO₂)) have already been measured inside vehicles compared

to the kerbside (Clifford *et al.*, 1997). By the time the pollutant has reached the kerb, it may have been substantially diluted - due to a combination of turbulent mixing and reaction. Thus, although any concentration of H_2S , moving from the point of emission, could be reduced over a few seconds before it is measured at the roadside, it could still be subjecting following drivers to a more polluted slipstream within a shorter time scale.

Close to major roads, the average concentration of hydrogen sulphide is therefore probably low, but significant peaks might still have a detrimental effect on crops, people and animals close to the point of emission, particularly drivers of other vehicles, pedestrians and cyclists. Ironically, as well as those with respiratory problems, physically active persons, such as agricultural and other outdoor workers would appear to be at greatest risk (Natusch and Slatt, 1978). In addition, the toxic effects of H_2S may increase following exposure to and/or consumption of alcohol (Lenga, 1988) or in the presence of other gases such as carbon di-sulphide (CS_2), carbon monoxide (CO), carbon dioxide (CO_2) and ammonia (NH_3) (Natusch and Slatt, 1978). Such gases are potentially present in motor vehicle, or agricultural, environments.

1.3 SUMMARY AND OBJECTIVES

Whilst a reasonable amount appears to be known, largely from industrial accidents, about acute hydrogen sulphide poisoning, little appears to be known about the effects of low level chronic exposure. However, there is an increasing body of opinion that H_2S could have a more deleterious effect upon the human body than has previously been acknowledged. Commercial instrumentation has tended toward providing personal monitors, with alarms, to warn workers of exposure to dangerous concentrations of H_2S of typically 20 ppm and above. However, low concentrations of H_2S , up to 100 ppb are receiving increasing attention by researchers, as will be discussed in Chapter 2. This study is therefore intended to

contribute to this knowledge by identifying possible sources of H_2S at these lower concentrations and by suggesting new techniques for their determination.

To monitor H_2S in the environment, and thereby identify possible causes of health effects, a two-way approach is required. Firstly, it is necessary to be able to measure low concentrations of H_2S over prolonged periods, to determine background concentrations and to measure any average elevation locally above that background. Secondly, it is necessary to confirm the nature of any short term variations, in particular any peaks of higher concentration, which might be being integrated to provide that local average elevation in concentration.

Hence the following objectives were set:-

- to determine whether Hydrogen Sulphide (H_2S) emissions from motor vehicles contribute significantly to air pollution compared to H_2S emissions from agricultural and other sources,
- to measure H_2S levels in the atmosphere, with particular reference to roadside sites,
- to investigate the relationship between peak, and long term average, H_2S concentrations,
- to investigate new technology suitable for the measurement of rapidly changing ambient concentrations of H_2S .

Chapter 2: LITERATURE & TECHNOLOGY REVIEW

DETERMINATION OF GASEOUS H₂S CONCENTRATIONS

2.1 ANALYTICAL METHODS

Methods for the detection and measurement of hydrogen sulphide date back at least 50 years. For the purposes of health and safety, the detection of dangerous concentrations of H₂S in the workplace is often sufficient, without necessarily knowing the concentration. All detection methods may be divided into two categories: those requiring mechanical aspiration and those which rely upon passive collection. Both categories may be sub-divided into those in which the adsorbent, or reactant, is either 'wet' or 'dry'. A summary of the principal methodologies is given in Table 2.1 at the end of section 2.1.

2.1.1 'Wet Active' collection methods

Methods in this group typically employ an electrical or mechanical pump which is used to draw gas through a solution which acts as a zero sink for H₂S. The solution may then be assayed using colorimetry, fluorimetry, spectroscopy or titration. Calibration is usually achieved using standard solutions of sodium sulphide (Na₂S.9H₂O) in a sodium hydroxide (NaOH) matrix.

For example, the 'methylene blue' method for the colorimetric determination of H₂S has been widely used (Jacobs *et al.*, 1957). The term 'methylene blue' has become a generic name for a number of similar methods where sulphide is captured in an alkaline solution and developed to form a blue colour which is measured colorimetrically. Typically this method captures H₂S in a suspension of alkaline cadmium hydroxide (Jacobs, 1965; Harrison and Perry, 1986). The resulting precipitated sulphide is converted to the methylene blue complex using N,N-

dimethyl-*p*-phenylenediamine (DPPDA) and ferric chloride (Fe_2Cl_3). (This method will be described in more detail in Chapter 3.)

However, collection methods using a solution of sodium hydroxide, including the methylene blue method above, were shown to be unreliable due to the oxidation, or photo-decomposition, of the sulphide in solution (Barnesburger and Adams, 1969; NIOSH, 1977; NIOSH, 1994). Nevertheless, this method is attractive due to its simplicity, its use of chemicals of lower toxicity than some of the alternatives which are described below and the relative cheapness of colorimeters compared with other instrumentation. A number of experimenters have therefore attempted to improve the stability and accuracy of the methylene blue technique by modifying the absorbing solution. The American Public Health Association Intersociety Committee for Manual Methods of Air Sampling and Analysis (1977) added arabinogalactan (commercially known also as STRactan 10) to their solution to minimise photo-decomposition. They were able to measure between 1 and 100 ppb using the revised method, for a 2 hour sampling period.

Purdham and Yongyi (1990) demonstrated that the stability of the solution, and therefore sampling times and sensitivity, could be greatly increased by adding triethanolamine (TEA) and ethylenediaminetetraacetic acid (EDTA) to the collection solution (0.1 M NaOH). Solutions containing both reagents were found to lose less than 5 % sulphide over 10 days, compared with previous sampling techniques where as much as 10 % loss was experienced in only a few hours. Their solution was also seen to be stable under normal lighting conditions.

A similar study (Balasubramanian and Kumar, 1990) used EDTA in solution with NaOH and zinc acetate. In this case the solution was found to be stable for approximately 70 hours before rapidly degrading by 70 % over a further 70 hour period. It was claimed that the presence of the EDTA in the alkaline solution stabilised the sulphide by masking trace contaminants (eg Fe^{III} , Mn^{IV}) that could catalyse oxidation.

Shanthi and Balasubramanian (1996) also employed a modified zinc acetate trapping solution for H_2S which was then analysed colorimetrically after stabilisation with gelatin and thiocyanate. A comparison was made with the methylene blue method and the results were found to agree very closely.

Koh *et al.* (1990) attempted to eliminate errors due to oxidation and photo-decomposition by converting the captured sulphide to thiocyanate in reactions with iodine and cyanide. Their method was successfully applied to the determination of sulphide in natural water samples but may be adaptable for the determination of hydrogen sulphide in air. A significant disadvantage of this method, however, is the use of cyanide.

Diarova *et al.* (1983) compared a photo-colorimetric methods using DPPDA (ie a 'methylene blue' technique) or silver nitrate (AgNO_3), with a colorimetric method involving two different gas analysers. For the comparison, a standard gas calibrator was used to produce H_2S concentrations similar to those found in the field. The results obtained showed considerable differences between the three approaches. The DPPDA method however, provided the closest agreement to known concentrations.

A fluorescence method for the determination of H_2S in air was developed by Axelrod *et al.* (1969). Following active collection in an alkaline solution, samples were subsequently treated with a solution of very dilute fluorescein mercuric acetate (FMA). The quenching action of sulphide in the sampled solution produced an inverse linear relation with fluorescence. The method has the advantage of simplicity and can be used to measure background concentrations as low as 0.2 ppb H_2S . Unfortunately, as with the methylene blue methods, the sulphide suffers from instability within the NaOH. Therefore sampling and analysis must both be carried out within a few hours.

Active collection methods using solutions in bubblers have inherent problems.

They are cumbersome, they need lengthy, preparatory and post-collection, analytical procedures. They also require power and regular servicing. A sophisticated mobile atmospheric research laboratory (“MARL”), capable of continuous monitoring of atmospheric H_2S and mercaptans was developed by Tarver and Dasgupta (1995). This was built to monitor these gases in US oilfields and employed a porous membrane diffusion scrubber for the capture of H_2S in NaOH . The H_2S was then desorbed by acidification and measured with an on-board gas chromatograph. The MARL therefore was able to minimise degradation of the H_2S in NaOH and reduce all analysis times.

2.1.2 ‘Dry Active’ collection methods

In ‘dry active’ collection methods, the gas to be sampled is drawn across a solid surface, treated to adsorb H_2S . As with the ‘wet active’ methods, the collection medium may then be assayed using colorimetry, fluorimetry, spectroscopy or titration. Calibration is achieved by a variety of methods depending upon the collection technique - including the use of standard solutions of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as described in section 2.1.1. The methods may also be divided into those which measure the average concentration over the sampling period, and those which can simply detect that a given average concentration has been exceeded.

Paper tape methods, where the sample gas is passed through an impregnated tape made of an appropriate filter material, are still employed in commercial instrumentation (see section 2.2). The paper tape is moved periodically so that a new section receives the sample gas stream. The paper tape is then either ‘developed’ chemically to produce coloured spots, or these may appear spontaneously during exposure. In either case the measure of discolouration is linearly proportional to the target gas concentration. Paré (1966) investigated the lead acetate impregnated tapes then in common use, and concluded that they were not suitable for long period sampling - such as occurs in air pollution work. He

developed a new mercuric chloride (HgCl_2) tape which he found more stable and suitable for the H_2S concentrations (1-10 ppb) he considered would be found in a city atmosphere. Paré also added urea to the HgCl_2 to improve the homogeneity of the spots produced. A drawback of this method is the highly toxic nature of mercuric compounds.

A different approach was taken by Buck and Gies (1966) who used glass beads in a glass tube through which the sample gas was passed. The glass beads were first coated with an equi-mixture of saturated silver sulphate solution (Ag_2SO_4) and 5% potassium sulphate (KHSO_4) and then dried in a stream of nitrogen. Hydrogen sulphide concentration was determined after a 30 minute sampling period. The H_2S was evolved in acid, collected in acidified ammonium molybdate and assayed colorimetrically as the molybdenum-blue complex. A modified version of this technique (Vadic *et al.*, 1980) used HgCl_2 on filter paper to collect the H_2S . This was found to be much simpler, and more stable - even after four weeks of sample storage - than the Buck and Gies (1966) method.

A similar technique, employing filter papers impregnated with silver nitrate (AgNO_3), was claimed to be capable of measurement of concentrations of H_2S as small as 5 parts per trillion (ppt) (Natusch *et al.*, 1972). The method of H_2S assay employed was sulphide fluorescence quenching of a very dilute solution of FMA, which had several similarities with that of Axelrod *et al.* (1969), previously described. The earlier method, however, suffered from the instability of the captured sulphide in the alkaline capturing solution, and this was avoided here. Unfortunately, in this method the resulting silver sulphide (Ag_2S) has to be dissolved using sodium cyanide (NaCN) - a highly toxic compound - as part of the analysis, prior to fluorimetric determination as before.

A review of impregnated paper methods was conducted by Natusch *et al.* (1974). They considered a number of methodologies including tapes impregnated with silver nitrate, di-cyanoargentate, mercuric chloride and lead acetate. Each method

was investigated considering possible modifying parameters such as humidity, light, flow rate, H₂S concentration, paper type, impregnation time and interfering gases. They concluded that Whatman No 4 tapes impregnated with silver nitrate were suitable for the collection of H₂S in concentrations from 1 ppb to 50 ppm.

As implied previously, there is an important difference between those collection techniques which can be used for continuous H₂S monitoring, those which can be used to determine mean concentrations over the length of a sampling period and those intended for health and safety monitoring where an immediate visible, or audible, indication of exceeding a preset limit is required. Prior to advancements in semiconductor and other electronically dependant technologies, visible methods based on colour changes were employed in each of the latter two categories.

British patent 1-084-469 (1967) describes a commercial instrument which simultaneously detected H₂S and SO₂. This is based on a technique (Summer, 1971) in which the air to be sampled is drawn through two glass tubes. One contains silver cyanide, using an inorganic solid such as aluminium trioxide as a carrier, to detect H₂S. The other uses a silica gel carrier for either phenol red or bromothyl blue, to detect SO₂. Exposure to the target gases causes a colour change which progresses along the tube as exposure continues. The length of colour change is therefore proportional to the total dosage.

Similar techniques are employed by other manufacturers for gas detection. Possibly the most common are disposable 'Draeger tubes' which are generally used, with a hand operated pump, to make a single measurement.

The Health and Safety Executive/ HM Factory Inspectorate (1976) published a method using Whatman No 3MM filter papers impregnated with lead acetate trihydrate. A 125 mL aliquot of the gas to be sampled is passed through the paper and the gas concentration determined by comparison of the stain produced with a standard colour chart. This technique gives an immediate indication of

concentration and is suitable for concentrations of H_2S from 5 ppm to over 40 ppm. Another similar technique (Graedel and Franey, 1979) uses the discolouration of lead-stabilised PVC. This method is capable of detecting the range of concentrations referred to in the HSE/HMFI document above, however the detection limit is determined by the exposure time. For example mean concentrations as low as 10 ppb may be measured if exposed for 15 hours. Although the higher concentrations referred to may be estimated by eye, the lowest concentrations require laboratory determination using a spectrophotometer.

Another self indication technique was suggested by Tarasanka *et al.* (1986). This appears to be considerably more accurate than those previously described in that it is claimed to measure concentrations of H_2S between 0.3 and 30 ppb. The method uses a glass tube containing silica gel impregnated with silver-gelatin complex. There is a colour change to steel-grey in the presence of H_2S which advances along the tube with increasing dose. The sensitivity of the method is partly dependant upon the geometry of the tube and the flow rate, 100 mL min^{-1} as published. It was found that the colour change was linear in the concentration range of 0-10 ppb H_2S . The only significant drawback appears to be the sensitivity of the impregnated silica gel to light, but this may be overcome by covering the tube with dense black paper during exposure.

The American National Institute for Occupational Safety and Health (NIOSH) has been active in promoting, and updating, methodologies for monitoring concentrations of pollutants. NIOSH method 296 (2nd Ed. 1980) for the collection and determination of hydrogen sulphide, uses molecular sieve, preceded by a dessicant tube containing sodium sulphate to remove water vapour, to collect any H_2S . A 5 L sample is taken and analysis is by means of a flame photometer. However, this method is only suitable for measuring concentrations of H_2S at their stated occupational exposure level (OEL) of 10 ppm and above.

Because of the low concentrations of H_2S normally found in ambient air, attempts

have been made to pre-concentrate the captured gas to make analysis easier and bring measurement within the range of pre-existing instruments. Fatkullina *et al.* (1979) used Polysorb 1 as a sorbent for H₂S and then subsequently analysed their samples using a gas-chromatograph in conjunction with a flame photometric detector (FPD).

A combination of molecular sieves Porapak Q (150-190 Fm) and molecular sieve type 5A (180-250 Fm) were used in series to collect gas samples in order to determine the composition of odorous sulphur based compounds suspected around a water reclamation works (WRW) (Roe, 1982). The results were again analysed using a gas-chromatograph in conjunction with an FPD. This technique was used to discriminate between H₂S and other sulphide compounds such as di-methyl sulphide.

Although semiconductors, and other contemporary electronic technology used for gas monitoring, will be primarily left for discussion in section 2.3 (Developing Techniques), certain 'dry active' detectors for H₂S have a sufficiently established history to warrant brief mention here. Commercially, there are a considerable number of aspirated H₂S monitors available which are aimed primarily at the safety and occupational health market. (Some examples will be discussed in section 2.2, Commercial instrumentation.) These are generally based on gold or metal oxide semiconductor (MOS) sensors. Smith and Shulman (1988) of NIOSH evaluated a number of MOS sensors for use in the concentration range of 0-110 ppm and found that, while they were suitable for safety purposes, there were a number of concerns which would limit their use scientifically for accurate monitoring of H₂S.

2.1.3 'Wet Passive' collection methods

Personal exposure monitoring for health and safety requirements relating to hydrogen sulphide has led to increasing interest in the use of passive instruments. Such devices need to be lightweight, unobtrusive and not require servicing during deployment. The modification of previously used active techniques is a logical step forward and a methylene blue-based method was proposed by Hardy *et al.* (1981). This method utilised a short section of tube, held vertically, with a membrane fitted at the lower end. The absorbing solution was retained by the membrane, and a stopper was fitted at the upper end. Hydrogen sulphide gas molecules permeating the membrane were captured in a sodium hydroxide based solution. The technique was found to be suitable over an eight hour exposure for a time-weighted-average working range of 0.1-20 ppm.

A personal monitoring 'badge' marketed by Du Pont uses zinc hydroxide solution to trap the H_2S and after an eight hour exposure period is analysed spectrophotometrically using a molybdenum blue method (Kring *et al.*, 1984). This 'Pro-tek' badge consists of a substrate 76 mm by 71 mm, with the solution contained in two 'blisters' on the outer surface. Exposure commences when the badge is removed from its sealed pouch, but only one of the blisters is exposed to the ambient air using an incorporated patented 'multicavity diffuser'. The other is used as a blank for comparison in the subsequent analysis and therefore experiences similar temperature conditions.

2.1.4 'Dry Passive' collection methods

A diffusion tube method for H_2S has been identified (Shooter *et al.*, 1995), suitable for measuring extremely low concentrations. Like the 'wet passive' collection methods above (section 2.1.3), this was based on previously described active techniques (Axelrod *et al.*, 1969; Natusch *et al.*, 1972; Shooter, 1993). The

researchers claim a detection limit of 50 ppt for a one week exposure. The method uses standard diffusion tubes containing either stainless steel meshes or circles of Whatman No 4 filter paper, impregnated with a mixture of silver nitrate, ethanol and glycerol.

Analysis after exposure uses the fluorescence quenching of FMA, as described before, to indicate sulphide concentration. An early suggestion of using the fluorescence quenching of FMA to measure sulphide was reported by Karush *et al.* (1964). However, it was not until much later (Shipchandler and Fino, 1986) that the correct molecular structure for FMA was determined. This might account for some stability problems experienced by the earlier authors.

This would seem to be a cheap and highly convenient method, but suffers from the necessity of using sodium cyanide to dissociate the sulphide from the silver, and the tendency of FMA solutions to hold dissolved oxygen. This can greatly modify the response and requires scrupulous care, including the purging of all laboratory ware with an inert gas such as nitrogen, during analysis.

Table 2.1 Summary of principal published techniques for the determination of hydrogen sulphide

Technique		Range	Resolution	Reference
Cadmium sulphide/ Sodium hydroxide	bubbler + pump	1 ppb - >200 ppb	1 ppb	(Jacobs <i>et al.</i> , 1957; American Public Health Association Intersociety Committee, 1977; NIOSH, 1977; Hardy <i>et al.</i> , 1981)
	passive (membrane)			(Deuchar <i>et al.</i> , 2002)
Lead acetate	Okita <i>et al</i>	2 ppb - 200 ppb		(Okita <i>et al.</i> , 1971)
	HSE	0-50 ppm but could be extended to ppb region with colorimetric analysis	~5ppm with eye or 1 ppm with colorimeter	(Health & Safety Executive and Factory Inspectorate, 1976)
	Pare			(Pare, 1966)
Silver nitrate	fluorimetric	~5 ppt	1 ppt	(Borovskaya, 1988)
	colorimetric	0.1-15 mg m ⁻³	0.1 mg m ⁻³	(Diarova <i>et al.</i> , 1983)
Micro-coulimetric titration by bromine		5-30 ppb	1 ppb	(Adams <i>et al.</i> , 1968)
Molecular sieve		depends on time & rate	14Fg/sample	(NIOSH, 1980)
Silica gel/silver gelatin complex		0-10 ppb		(Summer, 1971)

Technique	Range	Resolution	Reference
Silver cyanide (in tubes)	Depends on vol/time ~0-100 ppm		British Patent 1-084-469, 1967
Silver sulphate		9 Fg m ⁻³	(Buck and Gies, 1966)
Potassium sulphate	1-30 mg m ⁻³	1.4 Fg	(Vadic <i>et al.</i> , 1980)
Passive, silver nitrate etc in diffusion tubes	down to 50 ppt in 1 week	±0.1 ppb	(Shooter <i>et al.</i> , 1995)
Thiocyanate	3.2 - 192 Fg		(Koh <i>et al.</i> , 1990)
Zinc acetate	0-2 mg		(Balasubramanian and Kumar, 1990; SHANTHI and Balasubramanian, 1996)

2.2 COMMERCIAL INSTRUMENTATION

The list of commercial instruments, reviewed in this section, is not exhaustive. The products were selected to be suitable for the range of concentrations anticipated during the course of this project. They were assessed for their capability to measure, either mean concentrations of H_2S over several hours, or rapid fluctuations in concentration over a few seconds.

Ideally, the measurement of peak concentrations requires a rapidly responding instrument which is specific to H_2S and which is also portable, so that it may be carried within a motor vehicle for on-road measurements. On the other hand, for long term averages over a day or a week, roadside measurements can be taken with more cumbersome, and possibly mains powered, equipment.

Unfortunately, although cheaper than their bench counterparts, commercial portable instruments are typically aimed at the 0-50 ppm H_2S concentration range. These are intended for use as personal monitors and alarms in situations where a worker might be exposed to high concentrations. Great accuracy is not required under such conditions, nor is it necessary to discriminate completely between detected gases. More accurate and specific instruments - suitable for monitoring long-term mean concentrations - also tend to be more costly, have slower response times and be intended for bench operation.

In this study, the reduced sensitivity of the more portable instruments was offset by their more rapid response. The portable instruments also tend to be less specific to H_2S . For example, there are often cross sensitivities to carbon monoxide and benzene - both likely to be present in emissions from motor vehicles. These cross sensitivities can sometimes be compensated for by an appropriate combination of sensors, but this inevitably makes the instrument more costly. Instruments for the measurement of long term average concentrations, whilst needing to be much more sensitive to measure background levels accurately, can at least be placed in fixed

locations where it is easier to service power and other requirements. A summary of the instruments considered is given in Table 2.2 at the end of section 2.2.

The information in Table 2.2 has been taken from manufacturers' data sheets and personal communications. Certain items of equipment have either been demonstrated or borrowed for field trials. The results obtained are reviewed in the subsequent discussion on equipment and analysis techniques. (See Appendix A)

2.2.1 Electrochemical sensor based equipment

Electrochemical sensors for gas detection and measurement represent a fast developing section of the equipment market. This is due to the parallel demands for increased safety for personnel and for increasingly accurate measurement equipment for environmental monitoring. Although broadly categorised in similar terms in the preceding table, there are variations between sensors from different manufacturers, in regard to cross sensitivities in particular, and also in other factors such as temperature stability and inherent accuracy. There has been a marked increase in claimed sensor quality in the last few years.

Oldham Gas Toximeter for H₂S

The Oldham Gas Toximeter is based on City Technology sensors. The commercial instrument has a range of 0-50 ppm, with a resolution of 1 ppm. Casella London Ltd loaned a specially calibrated instrument with 0.1 ppm resolution. After switch on, a fifteen minute settling time was allowed and the instrument taken on numerous car journeys, of variable length and with differing weather conditions, during which many H₂S incidents were noted, by smell, by the vehicle driver and passengers. At these times the Oldham Gas Toximeter indicated changes in concentration of a maximum of 0.3 ppm, but due to significant cross sensitivity to

other exhaust gases, it is arguable how much of this was due to H_2S . Rarer negative excursions of down to -0.2 ppm were also recorded which may have been due to the NO_2 cross sensitivity indicated in the instrument's specification table.

2.2.2 Volatile Organic Compound (VOC) and related detectors

Equipment of this type is generally based on flame ionisation (FID) or photo-ionisation (PID) detectors. The former type uses a burning flame - typically hydrogen fuelled - to ionise the incoming, pumped, gas stream. The latter type uses a UV lamp instead of the flame and both types use either a silicon detector or a photo-multiplier (PM) tube. These methods are not gas specific and will detect any gas falling into the measured ionisation range. Depending on the target gas and the relevant environment this may not be a problem. However, vehicular hydrogen sulphide emissions are likely to coexist with benzene and many other compounds. Many manufacturers offer 'add-on' portable gas chromatographs, but these tend either to be not sufficiently accurate, or add greatly to price.

UVIC Gas and Vapour Monitor (Enviro Systems)

An example of the UVIC PID-based instrument was loaned by Enviro Systems. It was taken on numerous car journeys along with a standard Oldham meter as described above. Although supposedly sensitive down to 10 ppb, no H_2S incidents were recorded. Many other peaks were observed on the inbuilt graphical LCD screen, but none corresponded with perceived odours. The Oldham Toximeter only had a 0.1 ppm H_2S resolution so comparisons of peaks could not be made.

2.2.3 Gas chromatographs (GCs) and other gas analysers

Apart from standard bench machines, there is now an increasing number of portable and semi-portable GCs available. The most portable, unfortunately, are also the least sensitive. GCs designed for fully portable operation typically have a sensitivity of only 100 ppb, which is no better than instruments based on electrochemical sensors, which are a fraction of the price. The only advantage of a portable GC, but a significant one, is therefore the gas specificity.

There is a small number of semi-portable GCs and other equipment types, which are essentially small laboratory machines. All are expensive but give 1 ppb resolution or better. Sampling times depend on resolution but vary from 1 - 2 minutes.

An alternative approach to a dedicated H₂S analyser, is to use an SO₂ analyser preceded by an H₂S to SO₂ converter such as the converter marketed by Dasibi. This technique can produce accurate measurements of low concentrations of H₂S. For researchers who already have an SO₂ analyser, the purchase of a relatively cheap converter is a cost-effective alternative to purchasing another specialised analyser if portability is not an issue.

2.2.4 Other equipment

The range of monitoring equipment supplied by MDA Scientific uses a gas-specific, impregnated, paper tape through which the sample gas is passed continually. The discolouration of the tape, after a predetermined interval, determines the gas concentration. This is then displayed and can be relayed, via an industry-standard 4-20 mA interface, to separate recording equipment. The electronics then re-zero, and the same area on the tape is used repeatedly until discolouration becomes excessive and the tape moves to a new section. This procedure minimises tape

usage - especially at low concentrations. For hydrogen sulphide, two ranges are available, 0-100 ppb and 0-25 ppm, with sampling times of approximately 10 minutes and 10 seconds, respectively. The gap between these two measuring ranges typifies the technology gap, referred to earlier, between safety monitoring and environmental monitoring equipment.

The Jerome 631-X (Arizona Instrument Corp.,) is a portable H₂S monitor based on a gold film sensor. Readings can be taken individually on demand or at a set frequency. At the lowest end of the scale, the frequency is dependent upon the concentrations themselves - typically once every 15 seconds for concentrations of 1 ppb H₂S.

The reading is indicated on an in-built display and may also be sent via an RS-232 port to an independent data-logger or laptop computer. The instrument is intended for rapid, and convenient, monitoring around landfill sites or water reclamation works but is also suitable for roadside measurements.

Table 2.2. Summary of commercial instrumentation for the measurement of hydrogen sulphide

Manufacturer/Model		Range	Cost	Specific (y/n)	Response Time (95%)	Resolution	Calibration	Portability	Power	Logging?
UVIC		~ 10 ppb	£6k	n	0.5s	1 ppb	Not required	Excellent	Batt/mains	Yes 16k readings
Oldham	Gas Toximeter	100 ppb - 50 ppm	£200	+15% SO ₂ , (in range) +1%CO, (in range) -30%NO ₂ , (in range) -20%CL ₂ (in range)	<60s	100ppb	2 point	excellent	batt	no
	Gas Surveyor	As above but can have up to three sensors to counteract above cross-sensitivities								yes
MDA	SPM or TLD-1	0-100 ppb or 0-25 ppm	~£3-4k	y (depends on chemcassette)	depends on concentration ~10 mins @10 ppb	1 ppb	none	good	mains (or batt/mains inverter)	no but 4-20mA output
	7100 series	1 ppb - 50 ppm	£8k	y (depends on chem-cassette)	-"	1 ppb	none	poor	as above but with memory battery backup	4-20mA output, line printer, optional RS232,
ELE VOC detector	with GC	100 ppb	£7k	y	minutes	100ppb?		good	mains/batt	no but RS 232 output
Photovac	Snapshot	0.1 ppm		y	~60s			excellent	batt/mains	500 readings
	10S+ GC	0.1 ppb	£16k for H ₂ S, Full spec £19	y	~60s	0.1 ppb	permeation tube & calibrator	good	batt mains	2Mb ("1000's of readings")

Manufacturer/Model		Range	Cost	Specific (y/n)	Response Time (95%)	Resol- ution	Calibration	Portability	Power	Logging?
	AF21M (for SO ₂) with H ₂ S converter	1 ppb	£9k5 for analyser £2k5 converter	y						
Misc. (Electro-chemical Sensors)	Envin	Commercially used above 100 ppb	~£40 ea	No but susceptibilities known and subtraction may be used between different sensors				excellent	batt	possible
	City Technology	Similar to Oldham Gas Toximeters and Surveyors above								
	Capteur Sensors	Similar to Envin above								
Quantitech	Dasibi 1408 analyser with H ₂ S converter	0-2000 ppb	£9k for analyser £3k for converter	y	8 sec lag time 95 sec rise time	1 ppb		poor	mains (2-300 W)	
	STX70 personal monitor	0-50 ppm	£350	As Oldham Gas Toximeters and Surveyors above - but waterproof						
Arizona Instruments Inc	Jerome 631-X	1 ppb - 50 ppm	£10k	y	20 sec for 1-100 ppb	1 ppb	'self calibrating'	excellent	batt/mains	yes, via RS 232 output

2.3 DEVELOPING TECHNIQUES

Sensor technology is a constantly advancing aspect of science. Increasing health and safety demands imposed on industry by both the legislature and the threat of litigation, mean that new sensor development is a high priority in many fields. This section describes some of the latest techniques to be applied to H₂S detection, and those which show promise for the future. A summary of this equipment is shown in Table 2.3 at the end of section 2.3.

2.3.1 The electronic nose

The idea of an ‘electronic nose’ (Corcoran, 1993) has been of particularly interest to the food industries as a means of quantifying the concepts of personal taste and smell. A group of different sensors - each of which need not necessarily be gas-specific - is mounted together in the same sample chamber. The gas mixture under scrutiny is introduced, and the readings from all sensors simultaneously monitored.

Detection is achieved by means of ‘training’ the array, using neural network software in an attached computer. The corollary of this is that the individual sensors do not need to be sophisticated or expensive types (Corcoran *et al.*, 1993). To train the array, single gases, or mixtures of gases in accurately known proportions, are monitored in the sample chamber and the outputs of each sensor recorded. The gas concentration, or mixture proportions, are then changed and a new set of readings obtained. This procedure is repeated numerous times, but in each case the data obtained is fed back into the computer concurrently with each new data set and compared with the known proportions existing in each case. Progressively therefore, the computer ‘learns’ by iteration which results will correspond to a given gas combination. The greater the number of data-sets, the more accurate these results will be.

It is advisable to condition the signal from each sensor separately (Corcoran, 1994)

to remove unwanted electrical ‘noise’ and to bring signal levels to within the range of the computer’s voltage input. This then ensures that the individual sensors are broadly matched against one another, despite differing sensitivities and response curves.

Although the greatest current interest in the electronic nose is in the food industry, smell and flavour are inextricably linked with gas composition. However, there is also interest in the use of the electronic nose for the detection of single gases. This is because most sensors have cross sensitivities to other gases which can interfere with the accurate reporting of results. The electronic nose, and its neural network, turns these cross sensitivities to its advantage because each sensor that has even the slightest cross sensitivity to the target gas is able to contribute to the resulting measurement. The electronic nose is therefore able to measure concentrations of gases for which no specific sensor has been designed.

The sensors used in the array can be of a variety of types (Corcoran and Shurmer, 1994), including standard, ‘off the shelf’ products, but the new concept of the electronic nose has run in parallel with the development of new sensor types which have also been incorporated in monitoring equipment designs. The remainder of this chapter will describe these newer types where there is some relevance to the detection and measurement of H_2S .

2.3.2 Surface Acoustic Wave (SAW) devices

Piezoelectricity is the phenomenon whereby an electrical potential is created as a result of distorting a quartz crystal. The most common, simple application of this is probably the domestic gas lighter. Conversely, the application of a voltage to the ends of such a crystal causes a distortion of the crystal and an appropriate regular voltage variation can cause the crystal to oscillate. If the excitation electrodes are placed either side of the crystal, this oscillation occurs throughout the crystal and

is therefore three-dimensional in nature. This is known as a bulk acoustic wave (BAW) (Nieuwenhuizen and Nederlof, 1992). A surface acoustic wave (SAW), as the name suggests, occurs only on the surface of the material and is therefore essentially two-dimensional. This form of oscillation has several advantages of which probably the most advantageous is that the frequency of oscillation can be increased without having to make the crystal substrate ever thinner, and therefore more brittle.

Surface acoustic wave oscillations are stimulated by means of an inter-digital transducer (IDT) (Nieuwenhuizen and Nederlof, 1992). This consists of interleaved metal electrodes at each end of the SAW substrate. The surface waves are induced by passing an oscillating current between the interleaved electrodes and the waves continue along the surface of the device from the ends. The oscillation frequency is not only dependant on the applied voltage waveform and the resonant frequency of the substrate, but also to any surface coating. Therefore, to turn this device into a sensor, a chemical or biochemical coating can be applied to the surface which is selectively sensitive to the fluid under investigation. Chemical or biological interactions change the frequency of oscillation, by changing the mass of the coating, and it is this change that is representative of the fluid under investigation.

In practice, an exposed IDT is placed alongside an unexposed IDT. Ideally these are formed on the same substrate so that any changes due to factors such as temperature variations may be minimised. The same substrate may also be used for more than one set of sensors to present a highly refined form of the electronic nose. Either a trained neural network or pattern recognition techniques - known as chemometrics - (Cranny and Atkinson, 1992) may then be used to determine the concentrations of the compounds of interest.

SAW devices have been used to measure concentrations of a variety of gases, such as hydrogen (D'Amico *et al.*, 1982), ammonia (D'Amico *et al.*, 1987) and nitric

oxide (Barendsz *et al.*, 1985; Hoummady *et al.*, 1991), as well as H₂S (Vetelino *et al.*, 1986; De Andrade *et al.*, 1989; Falconer, 1995; Galipeau *et al.*, 1995). SAW devices have also been investigated for a variety of other purposes - including their use as liquid, pressure and biosensors - the latter being described later in this section 2.3 (Bryant *et al.*, 1981; White, 1985; Hoummady and Hauden, 1992; Yakovkin *et al.*, 1994).

2.3.3 'Thin Film' sensors

Surface acoustic wave devices are generally constructed by applying electrodes to a chemically inert substrate. The sensitive layer is then applied to the whole surface. On the other hand, 'thin film' sensors have the sensitive layer applied directly to the substrate and the electrodes added on top.

This method of construction is particularly well suited to tin oxide sensors which are commonly used in gas detection. A drawback is that they have to work at an elevated temperature but a heater element can easily be integrated into another layer of the thin film sensor during construction (Bartlett and Gardner, 1992).

2.3.4 Langmuir-Blodgett (LB) films

Strictly speaking, Langmuir-Blodgett (LB) films are ultra-thin organic films deposited on a substrate by means of a particular process, but the term is now commonly applied to any film consisting of either a single molecular layer, or a number of superimposed, discreet molecular layers, however they are applied (Ulman, 1991a; Ulman, 1991b).

The films are created by manipulating the film material on the surface of a liquid in a specialised trough - in a similar way to that in which oil can be moved on the

surface of water using a paddle blade. When the film is of the desired shape and thickness, it is floated onto a substrate - typically by withdrawing the substrate upwards through the film.

These ultra-thin films are potentially useful as highly sensitive gas sensors. Currently however, they suffer from their great susceptibility to physical damage.

2.3.5 Electro-active polymers

Electro-active polymers (EP) are created by 'doping' the polymer material during production. Polymers manufactured in this way can be used in a variety of sensors including the SAW types mentioned above as well as optical, potentiometric and bio-sensors (Josowicz and Janata, 1993). They are especially well suited for use in resistive sensors.

The initial doping of the material of the polymer can comprise a number of different doping compounds for different purposes. The primary purpose is to make the sensor under construction sensitive and selective to the target compound. The target may be gas or liquid and, as polymers are chemically and physically robust, sensors based on EPs are inherently tougher than those made of LB films.

The secondary doping may then be used, for example, to enable improved conductivity.

2.3.6 Biosensors

Biosensors combine a biological component, typically an enzyme, with a transducer - which is generally a pair of electrodes (Chemnitius and Cammann, 1996). The fluid under analysis - which is generally a liquid rather than a gas - is immobilised

on the sensor at the molecular level, by a variety of methods which include covalent binding, adsorption, cross-linking and entrapment. Electrodes on the sensor are then used to convert these molecular changes to an electrical signal - typically by monitoring changes in conductivity.

The sensor itself may be as simple, and therefore cheap, as a suitably impregnated strip of filter paper, or may be more sophisticated using the thin-film techniques described previously or glass frits. Because of the way in which the bio-reactions occur, biosensors should be thought of as 'single-use' devices which are disposed of after analysis. A significant advantage of the biosensor used in this way, is that the sensor may be exposed to the target fluid before connection to the electrodes, and ancillary analysis equipment, which may be some distance away. The 'single-use' approach also avoids many of the usual problems associated with electrical sensors, in that long term stability, deterioration of the device and repeated calibration can be avoided by suitable batch production and quality control techniques.

The biosensor is currently being appraised primarily in the medical, and associated healthcare fields - but there is obviously considerable scope for future deployment as a passive gas sensor.

2.3.7 Fourier Transform Infra-Red spectroscopy(FTIR)

FTIRs are a highly sophisticated means of measurement. The equipment comprises two parts, a transmitter and a receiver, which may be mounted close together or long distances apart, and are a variant of a standard infrared spectrometer which yields an output signal as a function of 'spectral colour'. The FTIR may therefore be used to monitor multiple gas concentrations in a small cell in a laboratory, across a road or along the perimeter of a site by comparing the sample spectrum

with a database of spectral ‘fingerprints’. This is a highly sensitive, but expensive, technique.

Table 2.3 Summary of developing techniques for the measurement of hydrogen sulphide

Technique		Range	Cost	Specific	Time	Resolution	Calibration	Portability	Power	Logging?
Electronic Nose. To detect an “array” of smells & gas combinations.		~100 ppb upwards	sensors cheap but associated instruments currently expensive	no - but use of neural networks can make so	<1 min ?	?	via neural network “learning”	not at present	mains	yes
Langmuir Blodgett Films (under development)		~100 ppb upwards	high initial but low per unit	poor currently for H ₂ S but will probably improve	<1 min ?	?	gas calibrator	probably good soon	possibly battery eventually	probably
Biosensors										
Reactive films	Piezoelectric (bulk wave)	down to ppb, up to many ppm	low, 10's of £	y	seconds	+/- 5% full scale	gas calibrator	excellent	batt/mains	possible
	Surface Acoustic Wave (SAW)									
	Resistive									
	Thin Film									
FTIRs		down to ppb	expensive	y	seconds			poor	mains	yes

2.4 SUMMARY

The methylene blue assay method has been refined over several decades to determine ever smaller concentrations of H_2S in air. It was decided to attempt further refinements of this methodology as this seemed to offer the greatest number of opportunities over a considerable H_2S concentration range. These refinements were to include the development of an improved trapping solution and the investigation of possible passive techniques, and their application to measure ppb concentrations over periods of several days.

Techniques and instrumentation to track and record rapidly changing concentrations of H_2S were found to be in short supply both in the literature and from commercial sources. Although sensor development, and electronic conditioning for specific gases, appears to be going through a period of rapid development, no portable instruments at all were found to satisfy the requirements of this project. Therefore it was decided to develop a new instrument for this purpose.

Chapter 3: DEVELOPMENT OF THE DIFFUSION RESERVOIR

3.1 INTRODUCTION

The initial objectives of the project (section 1.3) were to measure H₂S concentrations as long-term averages and also as rapidly changing values. The literature and technology review (Chapter 2) suggested that there were no proprietary methods, nor commercial instruments, which were able to achieve both of these measurements using portable equipment. Therefore, it was decided to use a different technique for each type of measurement.

This chapter is concerned with the development of a method for measuring long-term average H₂S concentrations over periods of several days. The following chapter (Chapter 4) describes a new instrument, developed for measuring rapid changes in H₂S concentration during periods of a few seconds.

The literature review (section 2.1.1) included a number of studies (Jacobs *et al.*, 1957; Jacobs, 1965; American Public Health Association Intersociety Committee, 1977; Harrison and Perry, 1986; Balasubramanian and Kumar, 1990; Purdham and Yongyi, 1990) in which the measurement of long term average concentrations of H₂S was achieved by capturing sulphide in solution and then using a variant of the methylene-blue method for sulphide assay. The measurement range quoted for these studies ranged from 1 ppb up to several ppm - depending upon the sampling period used and the type of exposure site.

A common feature of these techniques, is the drawing of ambient air through a solution by means of a pump. Hydrogen sulphide in the atmosphere is captured in the solution. At the end of the sampling period, the concentration of sulphide is determined using a colorimetric assay and the average gaseous concentration of H₂S then calculated from the volume of air sampled. The combination of capture, followed by methylene-blue assay, is simple, and relatively inexpensive, to perform.

3.2 METHODS

Some preliminary results in this project were obtained using the variant of the methylene blue technique outlined by the American Public health Association Intersociety Committee for Manual Methods of Air Sampling and Analysis (1977). The ‘midget impingers’, described in the published method, were replaced by larger ‘dreschel’ bottles and therefore the quantities of absorbing solution were increased in proportion. Precision 12 volt pumps (‘Constant-Flow Long-Period Sampler’ Model T13160, Casella London Ltd,), powered by re-chargeable ‘dryfit’ batteries, were used to draw in ambient air through three dreschel bottles in series. Each battery, pump and set of three bubblers was fitted into a box to make up portable aspirated collection units (ACUs) which could be easily and quickly set up on site (Figure 3.1).



Figure 3.1. Inside an aspirated collection unit (ACU). This holds three dreschel bottles, connected in series and containing absorbing solution, a precision pump and a battery.

Initially, it was not known how efficient the capture of H_2S would be and measuring the sulphide content, of the sulphide captured in each dreschel bottle, enabled the collection efficiency to be estimated.

The first experiment used dreschel bottles with plain tube outlets. These produced large bubbles and the presence of sulphide in the third (last) bottle indicated poor collection efficiency. Unfortunately, the pumps were inadequate to draw air through each series of three bottles when fitted with fritted pipes. Therefore, plastic caps with nine x 1 mm holes were used to reduce the size of the bubbles from the inlet tubes. Subsequent experiments showed that no sulphide reached the third bottle.

The ACUs were successfully used in several experiments to determine gaseous H_2S concentration alongside major roads. However, aspirated collection methods have several inherent problems. The apparatus is cumbersome, analysis requires time - consuming chemical procedures, before and after collection, and the equipment requires both power and regular (daily) servicing. Other collection methods were therefore sought as alternatives. In particular, it was thought that a passive, self-indicating technique would save time, and enable greater replication at more remote sites.

Calibration of the sulphide captured in solution used in a colorimetric method is easily achieved using sodium sulphide solution standards. Whilst this calibration method may be used to provide a reliable indication of the amount of sulphide captured, it does not take into account the collection efficiency of the bubbler method. The collection efficiency must therefore be determined separately, or a calibration made which includes capture and assay.

3.2.1 The chemistry of sulphide capture and methylene-blue assay

Jacobs' (1957) reviewed early attempts at using the methylene-blue colorimetric method for hydrogen sulphide assay and concluded that these methods suffered from oxidation of the captured sulphide. He described a comparison between two versions of the method. One version used a collecting solution containing zinc acetate, the other contained cadmium hydroxide. He concluded that whilst the latter solution captured in excess of 90 % hydrogen sulphide, the former captured less than 10 % and that the difference arose from different rates of oxidation of the sulphide in solution. The cadmium hydroxide version was later published as a 'Standard Method' (Jacobs, 1965).

Subsequently, Bamesburger and Adams (1969) used a cadmium hydroxide solution similar to that described above, with the addition of arabinogalactan ('STRactan 10') to the absorbing solution, to reduce photo-decomposition. The addition of arabinogalactan reduced that part of the sulphide loss attributed to photo-decomposition, from 95 % to 15-30 % over a 24 hour period. It is not clear how much of the sulphide loss was attributable to other factors, nor what they might be.

The methylene-blue method used in this project was based on that of the American Public Health Association Intersociety Committee (ISC) for Manual Methods of Air Sampling and Analysis (1977). This variant appeared in a review of H₂S sampling methods by Harrison and Perry (1986), and is similar to the method of Bamesburger and Adams (1969). Harrison and Perry (1986) noted that the ISC version of the methylene-blue method was only suitable for sampling periods of several hours, and also indicated that sampling and analysis should be carried out within 24 hours, to minimise photo-decomposition of the sulphide.

Other authors (Hardy *et al.*, 1981; Balasubramanian and Kumar, 1990; Purdham and Yongyi, 1990) also attributed sulphide losses primarily to oxidation of captured sulphide, and described the addition of ethylene-diamine tetra-acetic acid

(EDTA) and tri-ethanolamine as alternative ameliorating measures. These additions, in varying proportions, reduced sulphide losses by between 40 - 85 % over a 24 hour period.

Adaptation of the ISC method, to produce more stable collection solutions and combine the benefits of arabinogalactan, EDTA and tri-ethanolamine, had unforeseen problems. These required further modifications to be made before a reliable technique was established. The order of mixing constituents proved crucial to avoid a precipitate and the addition of ethylene-diamine tetra-acetic acid (EDTA) to the absorbing solution caused it to become acidified. However, this was rectified, using additional NaOH, to produce a collection solution with pH 11.9.

3.2.2 Analysis of sulphide captured in solution

A cadmium hydroxide based solution was used to capture sulphide and this was then assayed using the methylene-blue colorimetric method described below. This is summarised in Figure 3.2.

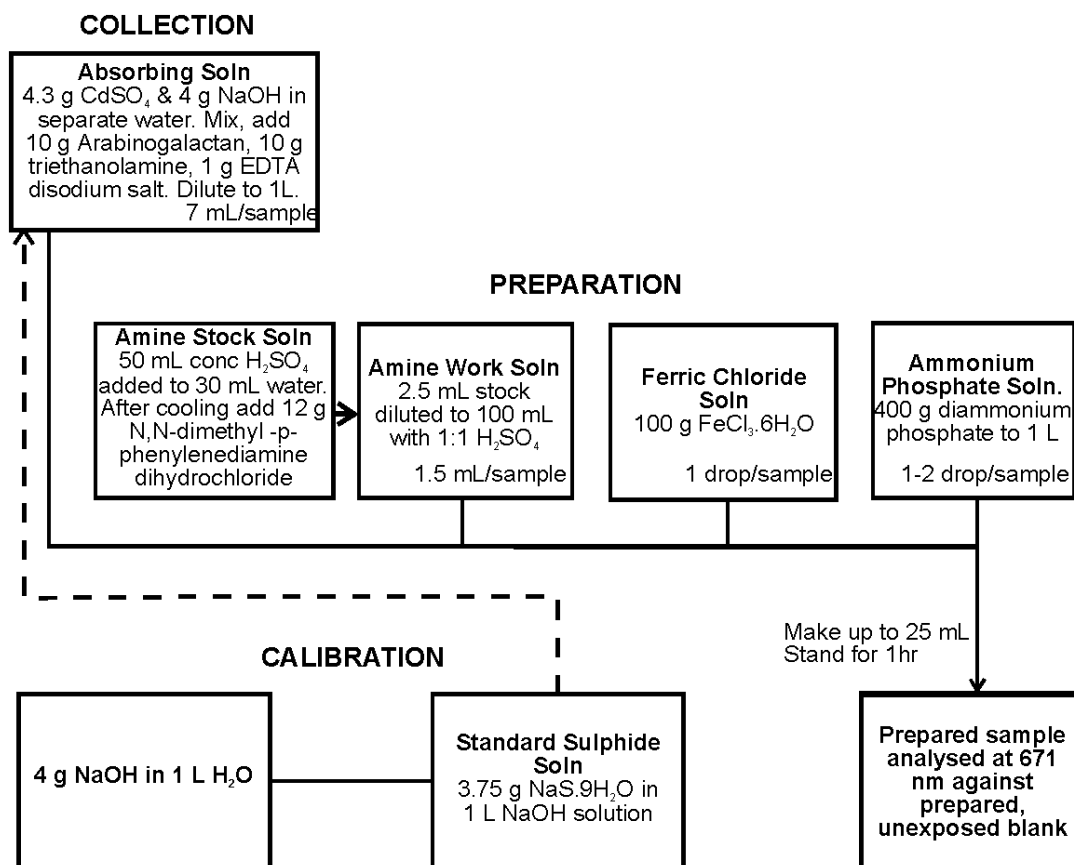


Figure 3.2. Summary of the Methylene Blue method used. Adapted from Harrison & Perry (1986), Balasubramanian & Kumar (1990) and Purdham & Yongyi (1990)

A capture solution was prepared by dissolving 4.3 g cadmium sulphate (CdSO_4) and 10 g arabinogalactan in separate 100 mL aliquots of de-ionised water and mixing these in a 1 L volumetric flask. Ten grammes of tri-ethanolamine (TEA) and 1 g of EDTA were then added with further mixing. Finally, 4 g of sodium hydroxide (NaOH), dissolved in a separate 100 mL aliquot of de-ionised water, was also added to the flask and the flask contents made up to volume with de-ionised water. It was found to be important that the constituents were mixed in this order to produce a clear solution, free from any precipitate.

An amine stock solution was prepared by adding 50 mL concentrated H_2SO_4 to 30 mL of de-ionised water. After cooling, 12 g of N,N-dimethyl-p-phenylene diamine dihydrochloride was added and the mixture stirred. A working solution

was prepared using 25 mL stock solution diluted to 1 L with 50 % H_2SO_4 .

A ferric chloride solution was prepared by dissolving 100 g ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$) in de-ionised water and making up to 100 mL

An ammonium phosphate solution was prepared by dissolving 400 g di-ammonium phosphate in de-ionised water and making up to 1 L.

A sodium sulphide stock solution was prepared from approximately 4 g of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) which was first washed in 100 mL ethanol and dried on filter paper to minimise the risk of contamination. A quantity of the dried salt (3.746 g) was dissolved in de-ionised water and the solution made up to 1 L. A working solution of 5.00 Fg mL^{-1} was prepared by diluting 10 mL stock solution to 1 L.

It was found that the sodium sulphide solutions had to be made up on the day required as the sulphide content degraded rapidly. The other reagents could be stored in a refrigerator for at least a month.

After exposure of the capture solution to atmospheric H_2S (in 7 mL aliquots), 1.5 mL of amine stock solution was added to each container, thoroughly mixed, and the contents washed through a funnel into a 25 mL volumetric flask, using de-ionised water. One or two drops of ferric chloride solution were added to the flask, which was then agitated, and two drops of ammonium phosphate solution added. The flask contents were then made up to volume, shaken and left for one hour in the shade for the colour to develop.

To calibrate the colorimeter, 0.5 mL, 1 mL and 2 mL of the sodium sulphide working solution were added to 7 mL aliquots of unexposed absorbing solution in 25 mL volumetric flasks and the colour developed in the same way as the samples from the exposed DRs. As previously discussed (Section 3.2.1), the sulphide

calibration standards were found to oxidize rapidly over time periods as short as 24 hours. Therefore a calibration graph was prepared for each day of assay. A typical calibration curve for the colorimeter is shown in Figure 3.3. On all occasions, the data points showed minimal scatter and followed very closely the straight line of the graph through the origin. This graph also indicates the overall linearity of the methylene blue method in its response to concentrations of H_2S .

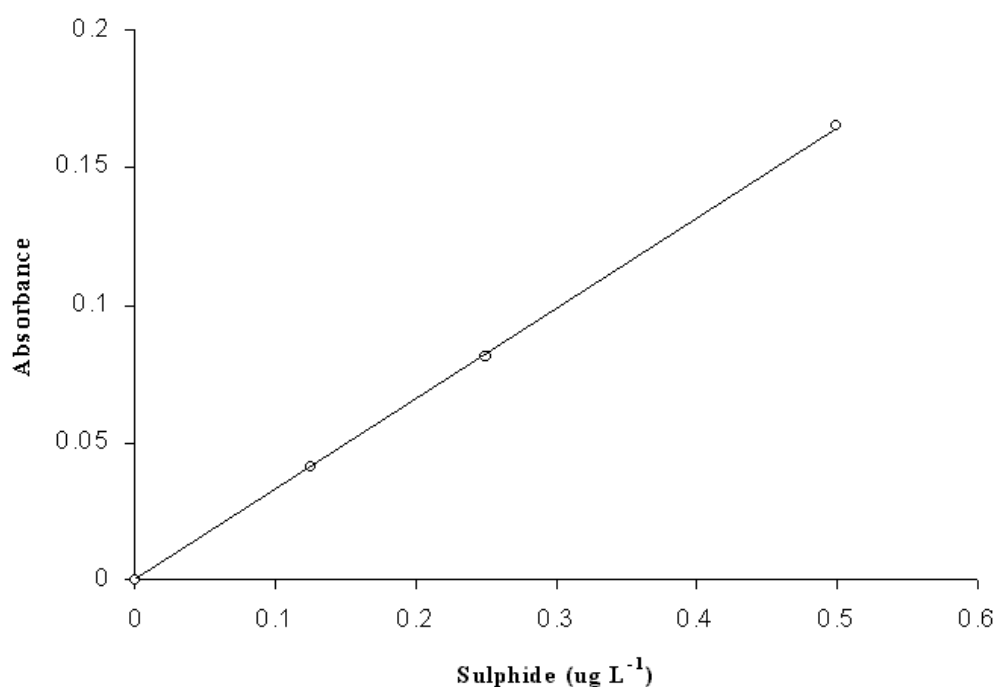


Figure 3.3. A colorimeter calibration showing a typical relationship between absorbance and sulphide concentration in solution.

A colorimeter (Jenway 6061, fitted with a 671 nm interference filter and a flow-through cell of 10 mm path length) was used to determine the absorbance of the contents of each flask. The absorbance of unexposed blanks was measured first and the colorimeter zero adjusted to the average absorbance of these. The relative absorbance of the solution from each of the other flasks was then determined, before re-testing the initial blanks to ensure that no instrument drift had occurred.

3.2.3 Comparison of results using different colorimeter filters

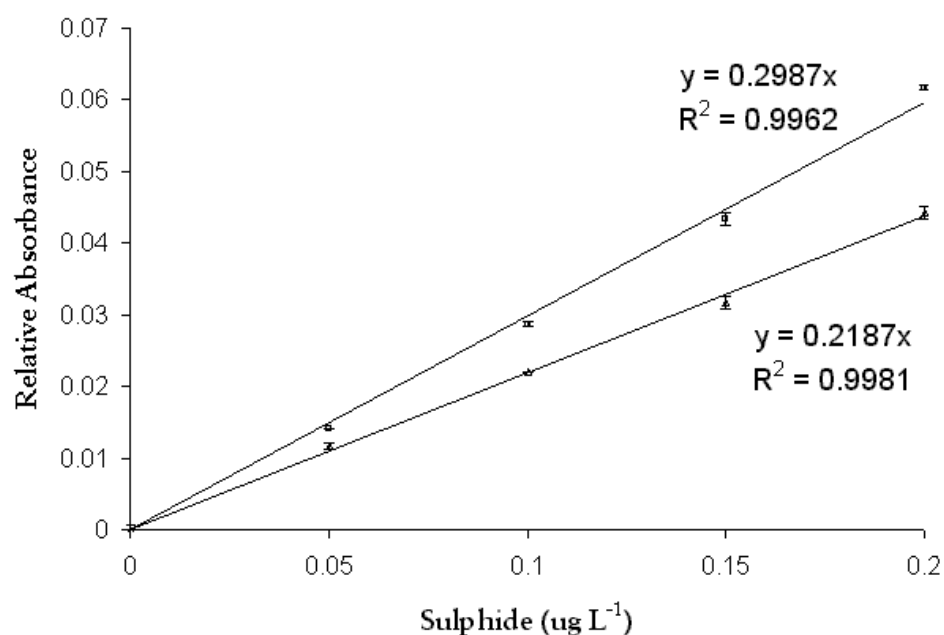


Figure 3.4 Comparison of absorbances using 671 nm filter (-) and 710 nm filter (|) on the same samples.

The ISC methylene-blue method (American Public Health Association Intersociety Committee, 1977) specifies that a 670 nm filter should be used for the colorimeter measurement. A 671 nm filter was borrowed to compare the response with the 710 nm filter initially available. The response was compared at the lower end of the working range where it was expected the greatest discrepancies might occur. It can be seen from Figure 3.4 that the 671 nm filter gave the larger response, by approximately 30 %, and therefore this filter was used in all subsequent experiments.

3.2.4 Stability of the collection solution

In order to determine the stability of the new solution described in section 3.2.2, before and after exposure to H₂S, an experiment was carried out to compare the absorbances of exposed and unexposed solution over time. The experiment was designed to indicate the changes, or degradation, of the collected sulphide from

day to day and also to indicate whether the age of the absorbing solution was a significant factor in any degradation.

Eighteen aliquots of fresh absorbing solution were prepared in 25 mL volumetric flasks. Six flasks were dosed with 0.5 mL of the NaS working calibration solution (as described in section 3.2.2). These were denoted 'high standard'. Another six flasks were dosed with 0.05 mL NaS (denoted 'low standard') and six with no sulphide added at all. A further group of six flasks contained similar aliquots of absorbing solution which had been made up one month previously. These also had 0.5 mL of the working calibration solution added to them on the same day as the others and were denoted 'old standard'. All 24 flasks were then flushed with nitrogen gas and stoppered prior to storage in a refrigerator.

The 24 flasks were divided into six sets of four flasks in order to determine changes in the four sulphide standards through time. Each set included one flask containing 0.5 mL of the NaS working calibration solution in fresh absorbing solution and one containing 0.5 mL of the NaS in one month old solution. The third flask contained 0.05 mL NaS in fresh solution and the last flask contained fresh solution but no added sulphide.

One set was assayed for sulphide on the first day. The other sets were then assayed at the same time on the five following days. The results from this stability test are shown in Figure 3.5.

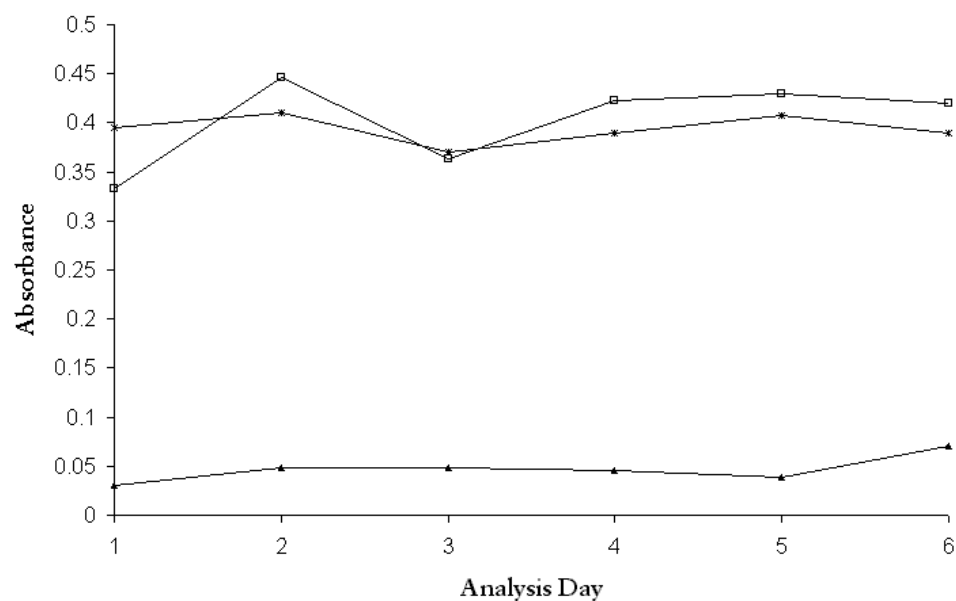


Figure 3.5. Degradation of different sulphide concentrations in absorbing solutions of different ages. - =high standard, < =low standard, i =old standard.

Fitting regression lines to Figure 3.5 showed that there was no evidence ($p>0.1$) of a trend with time in any of the sample groups. There was also no evidence ($p>0.1$) of difference between the means in the results from the fresh and one month old solutions. It can also be seen that degradation of the collected sulphide does not appear to depend upon the concentration of the sulphide captured.

3.2.5 The Diffusion Reservoir (DR)

A passive approach to gas monitoring has been suggested previously for sulphur dioxide (Reiszner and West, 1973) and subsequently adapted for hydrogen sulphide (Hardy *et al.*, 1981). This method has considerable appeal because of its simplicity and it was decided to attempt the same technique for H_2S , but to use the collection solution described in sections 3.2.1 to 3.2.4. Other changes to the method included the use of a more modern gas-permeable membrane. An

advantage of this approach was the availability of the necessary reagents, analysis equipment and familiarity with the assay technique due to its prior use with the ACUs.

Both Reiszner and West (1973) and Hardy *et al.* (1981) used a short glass tube with a removable bung at one end and a fixed membrane at the other to contain the collecting solution. This design was tried, but the membranes tended to become dislodged as the bung was fitted, so a simpler approach was adopted. A 10 mL polycarbonate sample vial, with a snap-on polythene lid, was used as the container. Celgard 2400 (Celgard Inc.) was identified as a suitable microporous membrane material. The pore size is sufficient to allow molecules of H_2S to pass through, but its hydrophobic polypropylene surface strongly inhibits any leakage of liquid water or loss of water vapour molecules. A 20 mm hole was punched in the centre of each lid and a 23 mm diameter disc of Celgard 2400 was cut from a sheet with a sharp scalpel, using a vial as a template, to make the membrane. The membranes therefore fitted to the edge of the vial and were held in place by the perforated polythene lids. No additional sealant was required and there was no contact between the absorbing solution and the polythene. The arrangement, which is referred to as a 'Diffusion Reservoir' (DR), may be seen in Figure 3.6.

The procedure for the analysis of the contents of the DRs differed only slightly from that described previously. Initially, the caps were removed from the vials with the membranes still in place. Using plastic forceps, the membranes were removed and pushed under the surface of the solution in the vial. Any drops of solution which leaked onto the cap were carefully rinsed into the vial using a small quantity of de-ionised water. Amine working solution (1.5 mL) was added to each vial and the membrane agitated to ensure thorough mixing and clearing of the membrane pores. The contents of each vial were then washed through a funnel into a 25 mL volumetric flask, using de-ionised water and the colour development procedure and colorimetric assay continued as before.

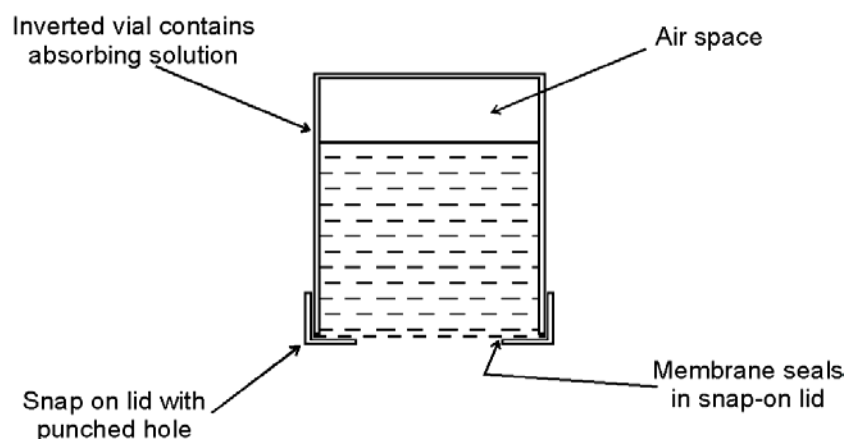


Figure 3.6. Construction of a Diffusion Reservoir (DR).

A gas calibrator (Monitor Labs Inc, model 8550), containing an H_2S permeation tube, was used in conjunction with an H_2S converter (Dasibi Inc, model 4109) and an SO_2 bench analyser (Analysis Automation Limited, model 477), to perform a calibration of the DRs for different exposure time periods and for a variety of gaseous H_2S concentrations.

At standard temperature and pressure, the H_2S concentration at the output of the calibrator is given by:-

$$\text{H}_2\text{S concentration (ppb)} = \frac{\text{permeation rate (ng min}^{-1}\text{)}}{\text{flow rate (L min}^{-1}\text{) } \times \text{ density (kg m}^{-3}\text{)}}$$

The DRs were exposed using the arrangement shown in Figure 3.7. The exposure box (Figure 3.8) had a quick release lid and the DRs were temporarily fixed to the base using Blu-tac. The lid was then replaced and the box carefully inverted so that the absorbing solution came into contact with the membrane surface. The gas flow rate through the SO_2 analyser was monitored throughout the exposure time.

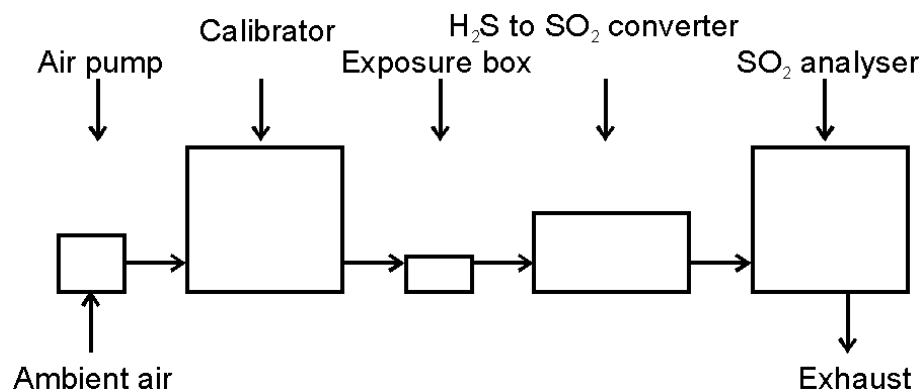


Figure 3.7. Dose response calibration layout

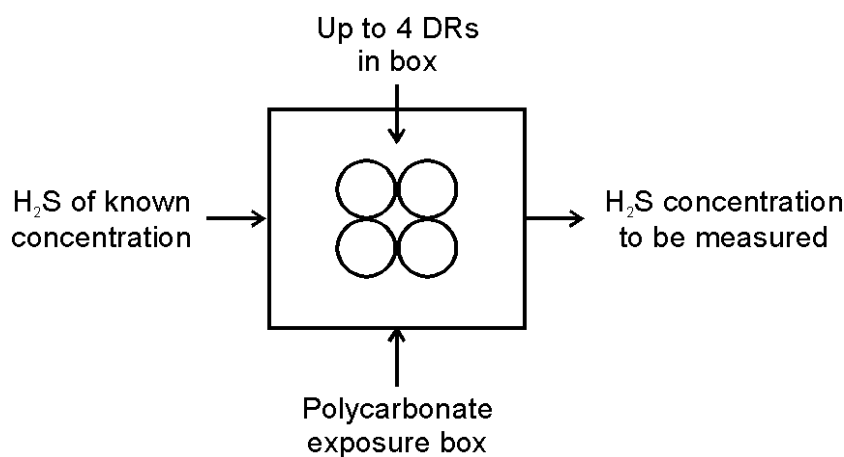


Figure 3.8. Layout of DR exposure box for dose response experiments

When no DRs were placed in the sealed box, the H_2S concentration reading on the gas analyser agreed with the theoretical H_2S output concentration of the calibrator. When DRs were fixed in the box as described, the reduction in the output reading of the SO_2 analyser was noted. In all cases, the analyser reading was reduced with the DRs in place in the exposure box, compared with no DRs, and a capture efficiency for the DRs was indicated of approximately 9 %. This was confirmed by measuring the total sulphide captured, and comparing it with the available sulphide in the gas volume passed through the exposure box during the exposure

time.

Each time the calibrator output was changed, the system was allowed to re-equilibrate for at least ten minutes before new samples were fitted in the exposure box.

For each data point, the dose (in ppb hours) was calculated by multiplying the exposure time by the gaseous concentration of H_2S present. The results of the calibration dose response experiments are shown in Figure 3.9 and are an amalgam of the data from a group of experiments in which the gas calibrator was used to provide different doses of H_2S to calibrate the DRs. This included different concentrations for a similar period of time and also the same concentration for different periods of time.

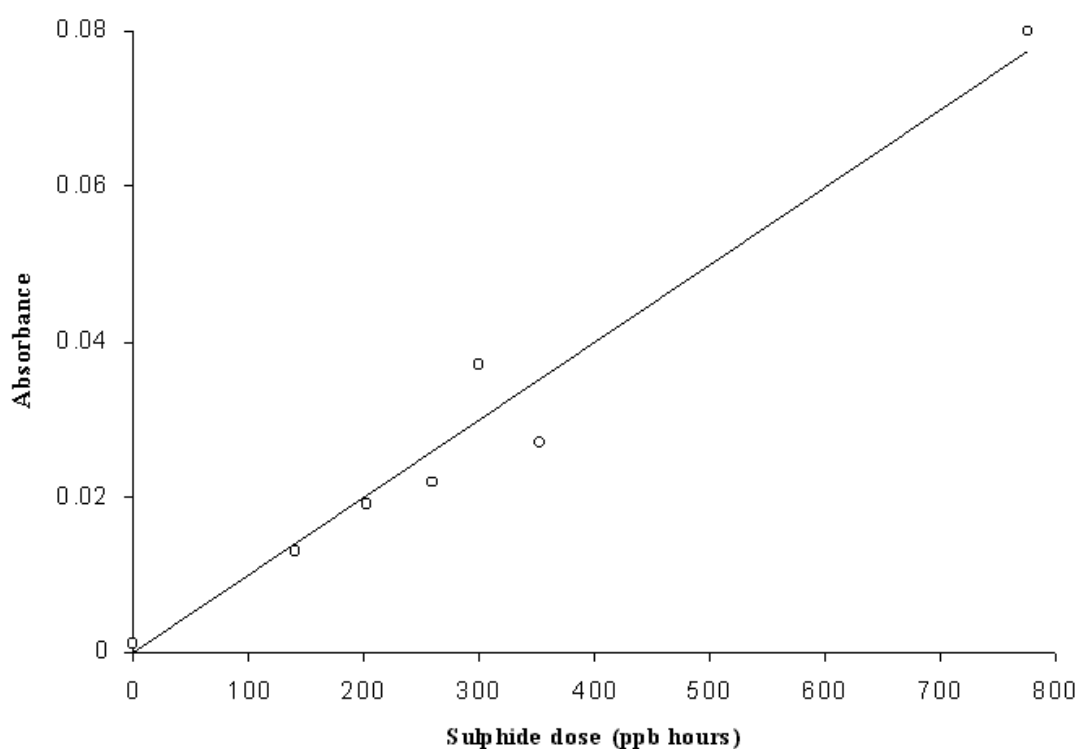


Figure 3.9. DR dose response curve

3.3 SUMMARY

The modifications made to the methylene blue method have resulted in a more stable solution, both before and after exposure, than that previously reported. The use of diffusion reservoirs (DRs) has also enabled this assay technique to be used in a cheap, passive manner for area and point monitoring in a variety of locations and over a large range of H_2S concentrations.

Chapter 4: DEVELOPMENT OF THE HYDROGEN SULPHIDE PEAK GAUGE (HSPG)

4.1 INTRODUCTION

Most modern monitoring equipment is based around a sensor producing an analogue voltage, or current, which is converted to a digital signal, at the earliest stage possible, for further processing. The advantage of this method is that, after the initial conversion, the resulting digital signal is substantially impervious to electrical noise, drift, minor changes in component values, temperature and supply voltage. In many cases, the final data output is easily passed to a computer for analysis by appropriate application software. Contemporary instrumentation therefore endorses the view that, in most cases, it is easier to develop digital technology to monitor and control processes, than it is to overcome the problems inherent in the manufacture of analogue components.

However, digital sampling of the analogue sensor output is discontinuous. In many situations this is not important but, if the sensor signal changes rapidly, data will be lost. If the digitisation occurs at a sufficiently rapid rate, then the large amounts of data recorded will oblige the digital designer to periodically, or continuously, average groups of measured data points. A specific example of this problem relates to very narrow spikes, or transients, incorporating changes of relatively large magnitude. Unless the digital sampling occurs exactly at the peak then only the rising or falling edge will be sampled, or the incident missed entirely. Automated digital averaging is likely to miss such spikes altogether.

If problems of drift and stability can be adequately controlled, or separated from the desired signal, then the output from an analogue circuit should follow the source with greater accuracy than the digital equivalent. Accordingly, the HSPG was designed with the intention of taking continuous measurements for several minutes at a time. With this system, some data loss will still occur at the end of

each measurement period, during reset of the instrument zero. However, the remaining data should provide a more accurate record of variation in concentration than a digitised signal.

In the early design stages, little was known of the variation and magnitude of the concentrations of H_2S to be monitored. The ability of a monitoring instrument to correctly track variations in actual concentration depends on the frequency response of the instrument being similar to that of the signal under investigation. Accordingly, as the characteristics of the variation in H_2S concentration are an important aspect of this study, it was decided that an error in absolute measurement in concentrations of $\pm 10\%$ was acceptable. This was considered an adequate compromise in finding a balance between extremely rapid response with poor accuracy, and a highly accurate measurement but with a very slow response. For example, the commercially available Jerome 631X is capable of ± 1 ppb resolution with an accuracy of ± 3 ppb at 50 ppb concentration, but can only take one measurement every 15 seconds at such low concentrations.

Concentrating on the variations in H_2S concentrations, rather than accuracy alone, would also enable greater attention to be paid to discriminating against electrical and electrochemical noise. The intention was to monitor the sensor output for as long a period as possible and then to re-check the zero of the instrument at intervals, using a source of H_2S -free air, to monitor any drift in sensor output. Ten minutes of monitoring, followed by one minute for a zero check, were initially considered sufficient for periods of data acquisition and to re-establish a zero point. Electronic constraints resulted in these figures being modified to 8.5 minutes and 40 seconds respectively.

From a review of literature, discussed in Chapter 2, it was decided to develop a resistive sensor using an H_2S -sensitive coating. The coating had to react rapidly, and reversibly, with variations in H_2S concentration and exhibit concurrent changes in conductivity. Two coatings discussed in the literature appeared to exhibit these

characteristics; both have been used extensively in the development of surface acoustic wave (SAW) devices as previously described (See section 2.3.2).

The first coating considered was tungsten trioxide (WO_3), but the technology in its production is highly specialised and beyond the capability of the workshop facilities 'in-house'. The second coating was a gel, consisting of a mixture of cadmium iodide, urea and glycerol (De Andrade *et al.*, 1989). This was readily applied in solution to the sensor surface using a glass rod. This approach has the advantage of simplicity, and replaceability, and was therefore adopted for the sensor to be described in the following section.

4.2 HSPG DESIGN

4.2.1 Summary

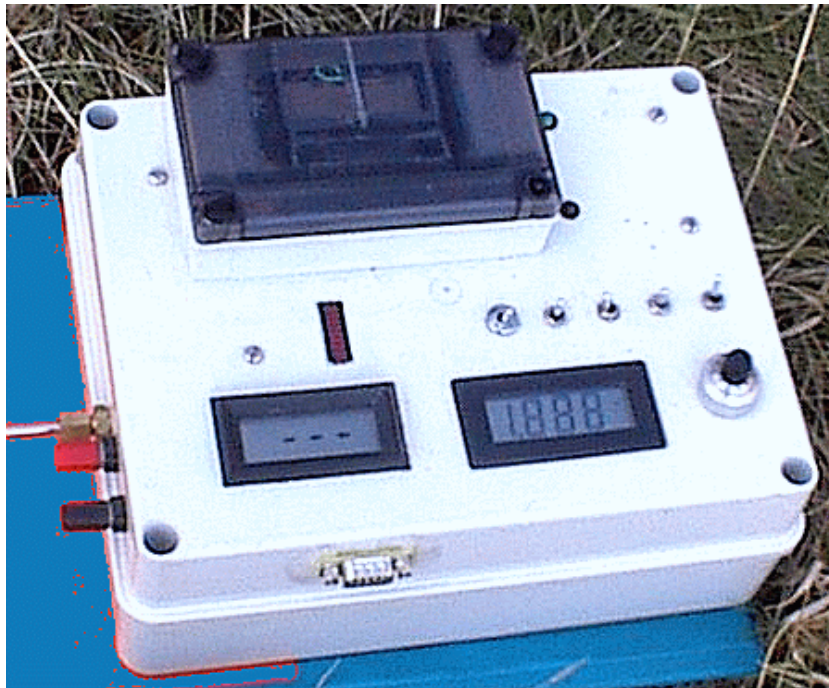


Figure 4.1 The completed Hydrogen Sulphide peak Gauge

The completed Hydrogen Sulphide Peak Gauge (HSPG, Figure 4.1) is a fully portable, and self contained, instrument designed specifically to measure rapidly changing hydrogen sulphide (H_2S) concentrations up to 200 parts per billion to within an accuracy of $\pm 10\%$. It uses an analogue resistive sensor coated with a chemical gel which is replenished every few days. The novel electronic design of the HSPG, circumvents problems of drift and electrical noise using a combination of unorthodox differentiating and convergent-zero techniques.

Calibration is achieved using a permeation tube in a gas calibrator or could be accomplished using a specialised gas source and a diluter. Controls are provided to enable display features, and facilitate setting up and zeroing. In normal use the HSPG will perform an automatic zero cycle approximately every 10 minutes, but this may be overridden manually if desired. The HSPG output is displayed in millivolts on a liquid crystal display (LCD) and also on its own mini, 8-bit data logger, based on a second LCD. Data may be downloaded to a computer from the internal logger via a serial port, but a further voltage output is provided to enable recording using a chart recorder, a more accurate external data logger, or an analogue to digital converter and laptop computer combination.

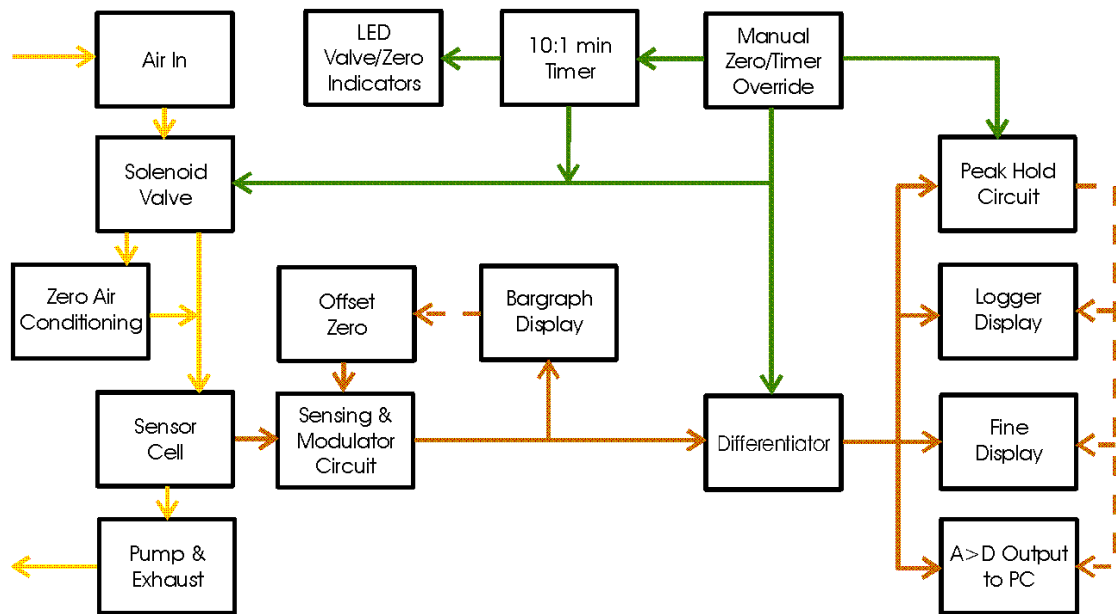


Figure 4.2 Block diagram of the HSPG connections. (Gas flows in yellow, control circuitry in green and signal routes in red)

A block diagram of the main modules of the HSPG are shown in Figure 4.2. These are discussed in detail in the following sections.

4.2.2 Sensor and headstage amplifier

The resistive sensor consists essentially of two electrodes, with a medium spanning them whose conductivity is responsive to the target. The conductivity is directly proportional to the cross sectional area of the electrodes, whilst being inversely proportional to their separation.

In the case of a gas sensor, the medium must respond rapidly to changes which will predominantly take place at or near the surface. To maximise the surface area available for reaction, and therefore the response, the electrodes comprise interlocking 'fingers' with the sensitive medium largely held between them (Figure 4.3).

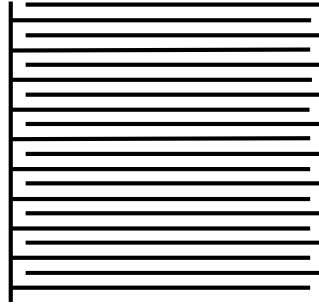


Figure 4.3 Gas sensor electrode layout.
(Approx 1.5x Actual Size)

The conductivity is therefore proportional to the total length of the edge of the electrodes, rather than their surface area, but inversely proportional to their separation, as before. Figure 4.4 shows a cross section through part of the sensor with the vertical scale exaggerated. Although the gel coating partially covers the copper strips, these areas are effectively shorted out by the copper and so do not contribute to the sensor resistance. It is only the resistance of the gel between the copper strips which is affected.

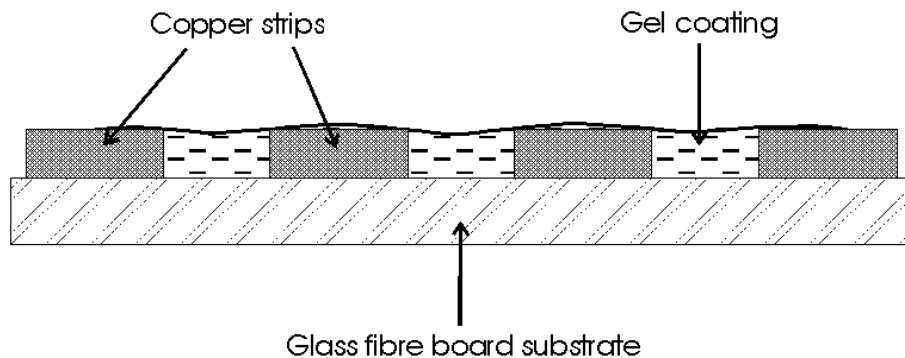


Figure 4.4 Enlarged cross section through gel coated sensor

To minimise the effect on the gel-coated sensor of errors due to factors such as varying temperature and humidity, a reference sensor was also used. The latter was placed in the airstream following the measuring sensor, but separated from it by a filter containing activated charcoal. The purpose of the filter was to absorb

hydrogen sulphide but to leave the airstream otherwise unchanged (Masuda *et al.*, 1999). The voltage output of the reference cell is subtracted electronically from that of the measuring cell so that the net output depends only on the incoming H_2S concentration. The general physical arrangement is shown in Figure 4.5. Because one electrode of each cell is connected in common with one electrode of the other, only three connections are necessary in all.

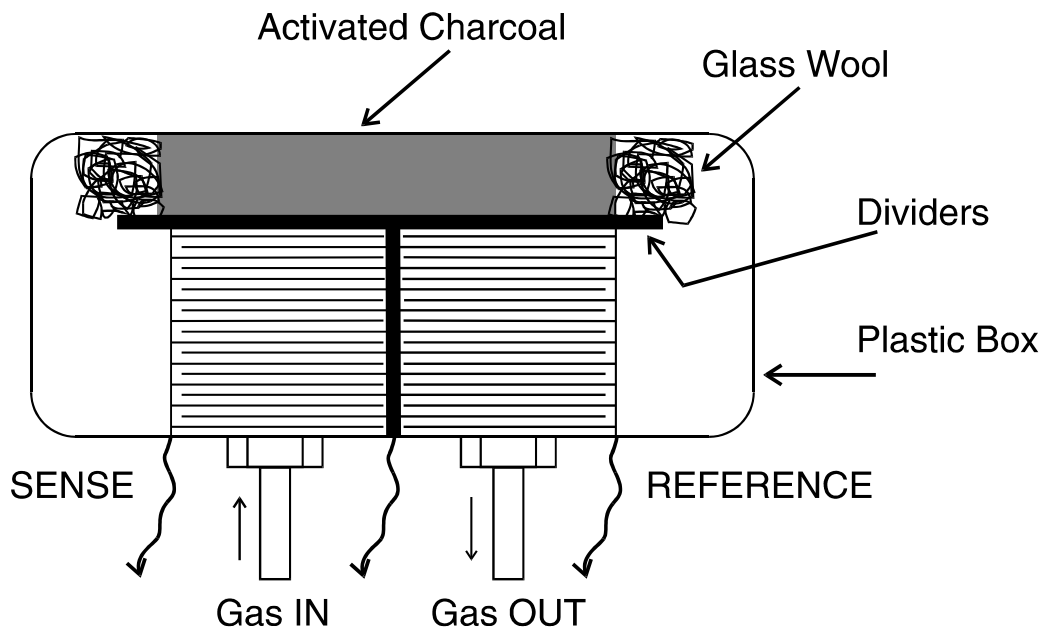


Figure 4.5 Prototype gas sensor for hydrogen sulphide, incorporating measuring and reference cells (Approx. Actual size).

The outputs from the prototype gas sensor in Figure 4.5 were amplified using a TLC271P operational amplifier (op-amp). Op-amps have two complementary inputs, one inverting (denoted '-') and one non-inverting (+). Feeding identical voltages into each input will therefore, theoretically, give a null output. The circuit employed with the prototype sensor is given in Figure 4.6. This is a standard 4-arm bridge. The purpose of the $100\text{ k}\Omega$ resistor is to limit the current through, and thereby the voltage across, the two sets of sensor electrodes. The $20\text{ k}\Omega$ trimmer sets the zero by balancing the bridge for a null output with both halves of the sensor exposed to zero concentration of H_2S gas. The $270\text{ k}\Omega$ feedback resistor

sets the gain of the circuit.

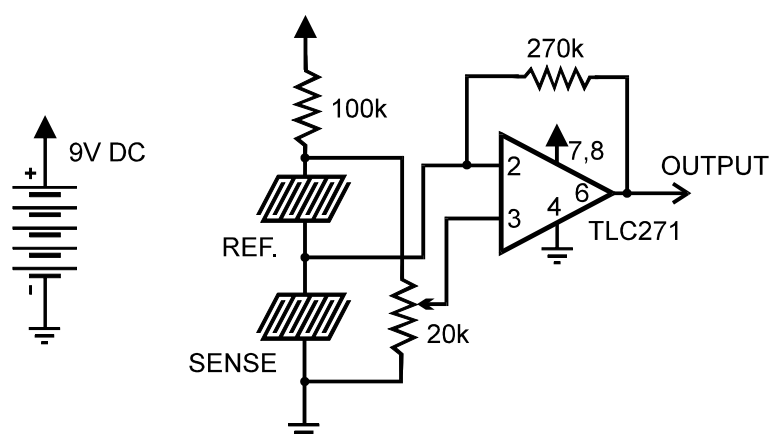


Figure 4.6 Circuit used with prototype gas sensor.

Although this circuit appeared to respond to H_2S when coated with the gel previously described, experience elsewhere (Pritchard, 1985) suggested that it is necessary to use an alternating current to supply the sensor cells, to avoid polarising effects within the gel. Therefore, the following additions to the basic circuit were devised which alternate the polarity of both halves of the sensor simultaneously, at a frequency of 50 Hz. The outputs of each cell need to be reversed at the same time, if the polarity of the output is also not to be reversed. This was accomplished using a 50 Hz oscillator to drive a series of three, single-pole, double-throw, CMOS switches. A large capacitor ($470\ \mu\text{F}$) was used to smooth the output of the stage and remove any switching spikes. Additionally, a 2.1 V precision voltage reference was employed to standardise the voltage across the sensor and replaced the $100\ \text{k}\Omega$ resistor in the previous circuit, as this resistor would make the sensor inherently non-linear. The final version of the headstage amplifier is depicted in Figure 4.7.

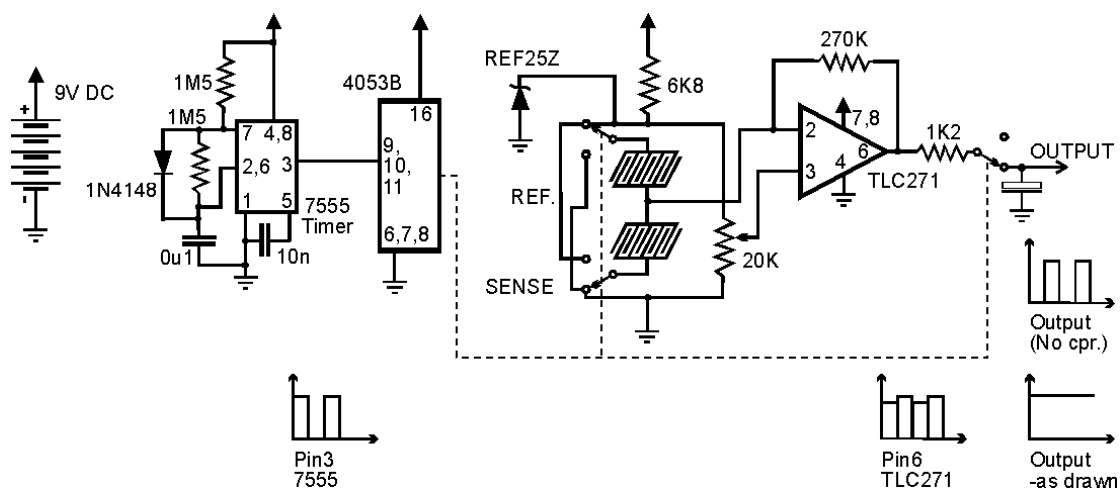


Figure 4.7 Headstage amplifier used with H₂S sensor.

4.2.3 The Differentiator

The differentiator is the key to stabilising the drift inherent in the use of a wet sensor in an input stage. As discussed previously (section 4.1), some baseline drift is acceptable in the context of a regular (10 minute) zero check and so a differentiator, in conjunction with a timer, is used to turn any drift into a flat baseline.

4.2.3.1 Differentiator circuit description

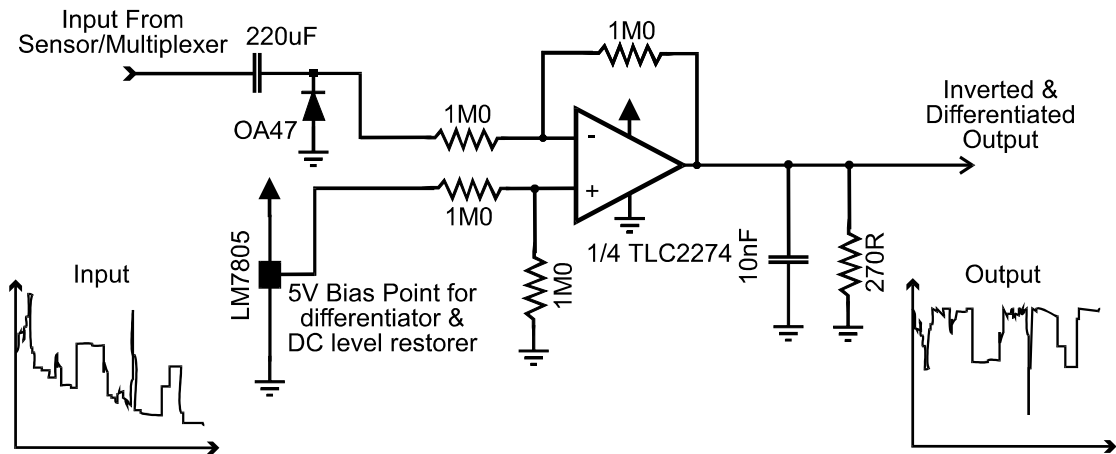


Figure 4.8 Differentiator circuit incorporating offset bias, single rail power supply and low leakage properties.

The novel circuit in Figure 4.8 is an adaptation of the conventional differentiator circuit (eg. Pippenger and Tobaben, 1985). Using the component values shown, this circuit permits any input variations, other than those deemed to be due to baseline drift, to pass through to the final output.

The 220 μF capacitor provides DC isolation, but allows voltages on the right hand side to respond immediately, in both direction and amplitude, to changes on the left. The following 1 MΩ resistor, however, limits the rate at which capacitor recharging can occur, but does not affect the output at the signal levels under investigation. Both this resistor, and those on the op-amp non-inverting input, and the OA47 germanium diode, are additions to the standard circuit. In the conventional circuit, the 1 MΩ op-amp feedback resistor is the sole factor limiting the current, which allows the right hand side of the input capacitor to recharge to the virtual-earth potential of the inverting ('-') input of the op-amp. In Figure 4.8 the extra 1 MΩ resistor between the capacitor and the inverting input of the op-amp, prevents the inverting input from immediately detecting the changed voltage on the capacitor as this potential difference will at first appear across the resistor. Instantaneously, the circuit will behave in the same manner as a unity-gain

inverting amplifier. The extra $1\text{ M}\Omega$ resistors on the non-inverting inputs act conventionally to minimise the common mode rejection ratio (CMRR). Since the op-amp inputs each have an input impedance of greater than $10^{12}\ \Omega$, and are therefore effectively infinite, as the right hand side of the capacitor discharges (or charges) through the input resistor, an identical current will flow through the feedback resistor creating a voltage on the output equal and opposite to that on the capacitor. The capacitor discharge is therefore not controlled by the feedback resistor, as in the conventional differentiator circuit, but by the input resistor.

The addition of an LM78L05 voltage regulator to provide a bias point for the non-inverting input is necessary since the differentiated output is an inverted image of the input. In a standard differentiator, a dual rail power supply is employed, allowing the output to become negative with respect to the supply ground. In the present design it was desired to operate from a single supply and so this biasing technique was employed. The inversion and DC bias is corrected in the Inverter/Buffer and DC Level Restorer stage which follows.

When the HSPG is calibrated and set up, there should be no negative voltage excursions from the output of the sensor stage. However, due to voltage droop, such excursions may still occur on the right hand side of the input capacitor of the differentiator. Any negative potentials here however, are limited to the 0.3 V forward voltage of the OA47 germanium diode. The germanium type was chosen in preference to the usual silicon, which has a greater forward conduction voltage of 0.6 V .

The output stage of the differentiator comprises the 10 nF capacitor and a $270\ \Omega$ resistor across the output. These are to suppress electrical noise and to provide an output load for the op-amp, respectively. The TLC2274 quad operational amplifier was chosen for its stability, low quiescent current, extremely high input impedance and ability to operate to 0 V with a single rail, low voltage supply.

4.2.3.2 Differentiator circuit action

It must be remembered that the prime purpose of the HSPG is not necessarily to measure steady state concentrations, but those which are subject to rapid change such as spikes.

Once switched on and allowed to stabilise as explained in section 4.2.1, a steady null voltage from the sensor will have no effect on the right hand side of the differentiator input capacitor whose output will also remain at 'zero'. To be strictly accurate, this will in fact be the 5 volt bias voltage, which hereafter is designated 0 V⁵.

From a steady zero state, if the input voltage rises instantaneously by an amount ΔV_L - as it will if the sensor experiences an instantaneous increase in H₂S concentration - then the voltage on the right hand side of the input capacitor, V_R , will rise by the same amount. If V_L remains constant, however, the magnitude of V_R will gradually diminish at a rate determined by the value of the capacitor, the value of V_R (always measured relative to 0 V⁵), the differentiator input resistor and leakages due to the capacitor's own internal resistance and op-amp input impedance.

If the initial positive change in V_L is followed immediately by a negative change of identical magnitude, returning V_L to 0 V, then V_R will also return to 0 V⁵. However, if there is a delay before V_L returns to zero then the magnitude of V_R will have diminished slightly. Nevertheless V_R will still fall by the same amount and the value of V_R will become negative relative to 0 V⁵. Once again, the magnitude of V_R will tend to diminish due to all the previously indicated factors, but in addition, the increasing forward conduction of the germanium diode will become of overriding importance as V_R approaches -0.3 V relative to 0 V⁵. This diode therefore minimises unnecessary negative excursions of V_R and also has an important role in ensuring that subsequent positive excursions can be more

correctly recorded. Its effect will counteract the continually drooping waveform for a series of spikes on the input, by returning the ensuing voltage waveform closer to its absolute value, each time the differentiator output attempts to fall below zero.

It can be seen that if any change in the input state is followed by a period without change, then V_R will tend to 0 V⁵. Paradoxically, this tendency towards a nominal zero is the crucial factor in not only ensuring a base line almost impervious from drift, but also in minimising voltage droop when the input contains narrow voltage spikes - due to the action of the germanium diode as previously described. Provided the rate of baseline drift is less than, or equal to, the rate of droop of V_R , then no change on the output will be observed. The time constant of the differentiator capacitor, and associated components, is critical in the operation of this circuit and the optimum values have been determined empirically.

In practice, the upper limit of voltage measurement, imposed by the voltages and amplifier gains of the circuitry, is for a +5 V step input relative to 0 V⁵. This corresponds to approximately 200-500 ppb H₂S as will be discussed later, in section 4.3.

Ideally, a succession of spikes and varied high and low concentrations of H₂S should always cause proportional changes in V_R . However, due to the capacitor voltage droop, and the action of the germanium diode, the value of V_R could approach either -0.3 V or +5 V relative to 0 V⁵ if the instrument were left indefinitely. Therefore, at the end of each zero-check period, the electronics should also be returned to zero state, by operating the output and peak monitoring reset switches as required.

A mechanical analogy of the operation of the differentiator is given in Appendix B.

4.2.4 Signal Processing and control

4.2.4.1 *The Bargraph Display*

The main function of the bargraph display is to assist in setting up the HSPG after it is first switched on. During monitoring, the display should also be checked periodically to ensure that the indicating LED appears in the lower half of the display during zero-air cycles. Adjustment should be made using the front panel zero, multi-turn potentiometer which should then be locked in position to prevent accidental movement. This procedure ensures that the differentiator, and hence the HSPG, can be used for the widest range of inputs by keeping the signal voltage central between the supply rails. The overall accuracy and calibration are unaffected because this control has no effect on output amplitude and because a manual zero is always made at the start of measurements.

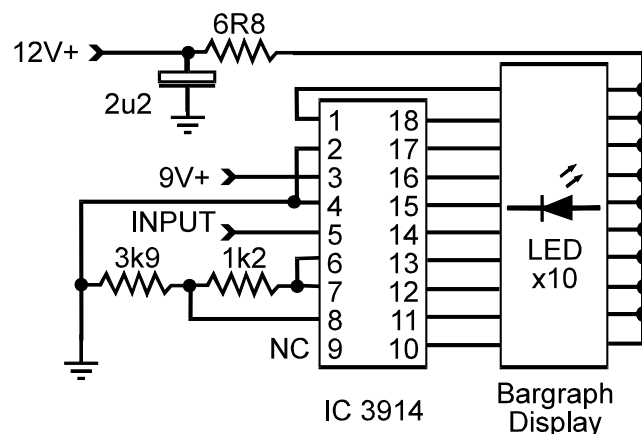


Figure 4.9 Circuit diagram of bargraph display for 0 - 5 V input

The circuit for the bargraph display is shown in Figure 4.9. The 3914 IC contains a potential divider chain, fed by an external reference voltage, and ten comparators - each of which drives a single LED in the bargraph itself. As depicted, only a single LED will be driven at any one time to conserve battery voltage.

4.2.4.2 *The inverter/buffer and DC level restoring circuit*

A standard unity gain inverting op-amp circuit was used, but configured as a differential amplifier (Figure 4.10). The non-inverting input was biased to the same point as that of the preceding differentiator circuit and this ensured that the output was free of any DC offset. The purpose of this circuit was to re-invert the waveform previously inverted by the differentiator and replace its reference, 0 V^Z , with the conventional 0 V line. This is extremely accurate, as any variations in tolerance of 0 V^Z are equally, but oppositely, reflected in the two stages and therefore effectively cancel out.

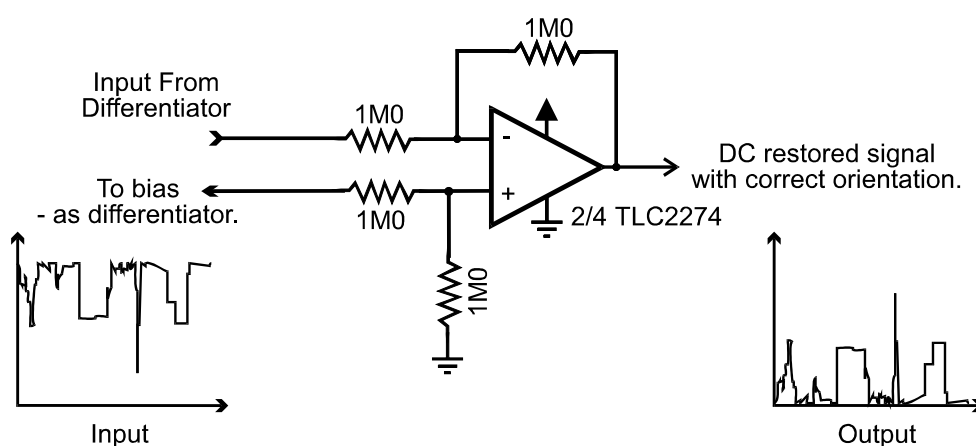


Figure 4.10 Inverter/buffer and DC level restoring circuit to correct inversion & level shift of preceding differentiator.

4.2.4.3 *The peak hold circuit*

A peak hold circuit is intended to measure the peak voltage of a varying input waveform - in this case equivalent to the peak H_2S concentration detected. The voltage is stored on a capacitor, but in a standard active circuit this suffers from 'voltage droop' due to the capacitor's own internal leakage.

The following circuit (Figure 4.11) is designed to minimise this effect and uses,

once again, high input impedance op-amps. Under test, this circuit, (Dale, 1985) took some forty minutes to droop 10% from an initial 8.03 volts - more than adequate for the current purpose. The second op-amp acts not only as a buffer on the output of the first, but also assists in error correction by using the voltage drop across a second diode to monitor the current flow on the first op amp output, which is a main constituent of leakage.

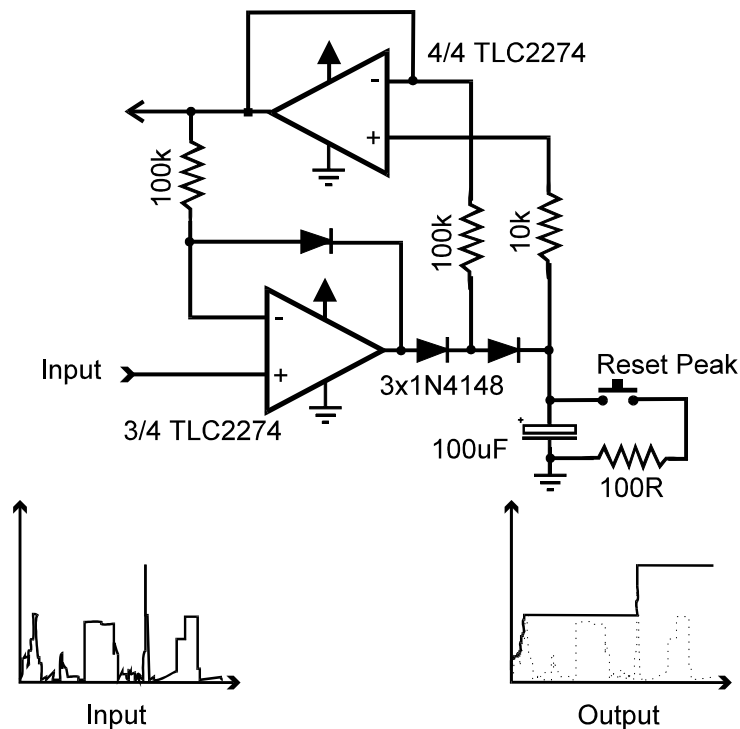


Figure 4.11. Precision peak hold circuit.

The circuit will continuously monitor the peak voltage recorded (effectively the peak H₂S concentration) until the 'Reset Peak' button is pressed. The current peak may be read at any time by operating the Peak Hold/Normal switch.

4.2.4.4 The timer and solenoid control circuitry

The integrated circuit which activates the three-way solenoid valve, controls the admission to the sensor of either ambient air, or zero-air. The circuit in Figure 4.12 is adapted from that used previously in a more complex sampling system (Micallef *et al.*, 1998) and conserves power by energising the solenoid valve momentarily.

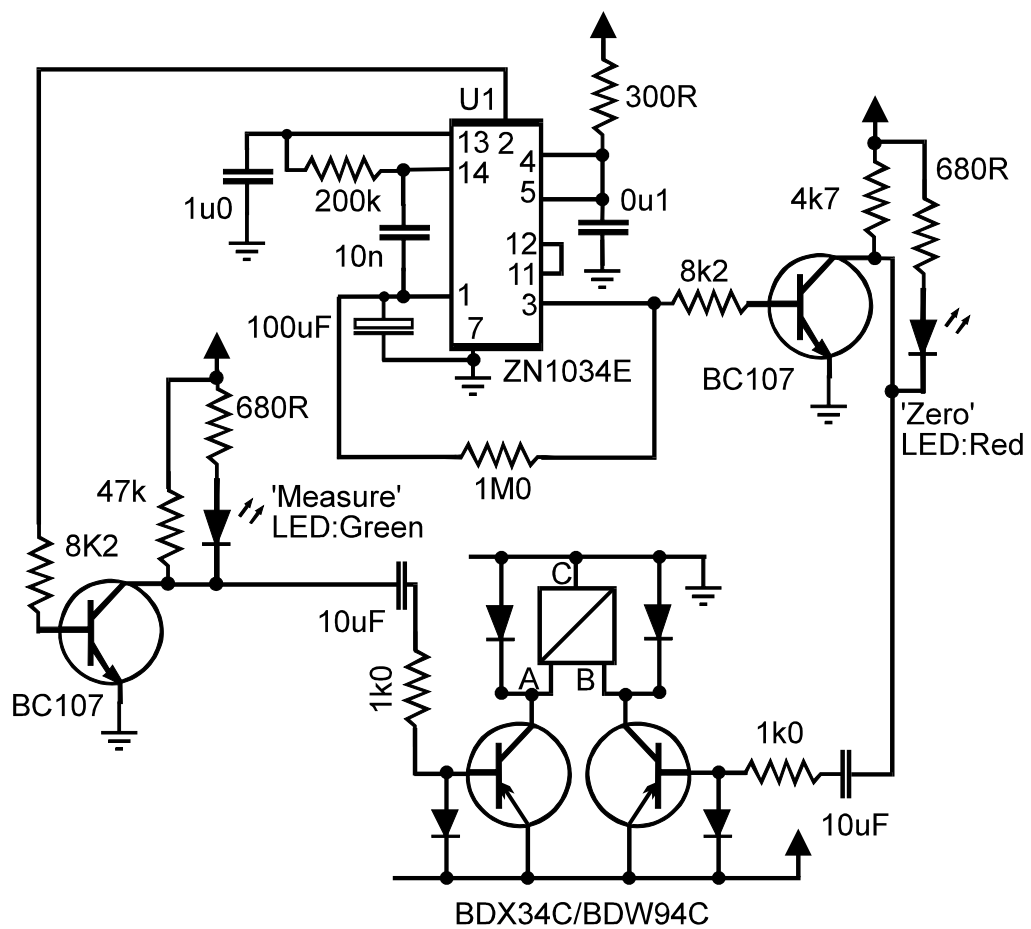


Figure 4.12. Auto-zero timer and solenoid driving and indicator circuit.

As well as controlling the solenoid valve, the timer also activates red and green indicator LEDs to show the valve status; green for sampling, red for auto zero. Either of these states may be overridden manually for setup, calibration or other testing.

4.2.5 Arrangement of pipework

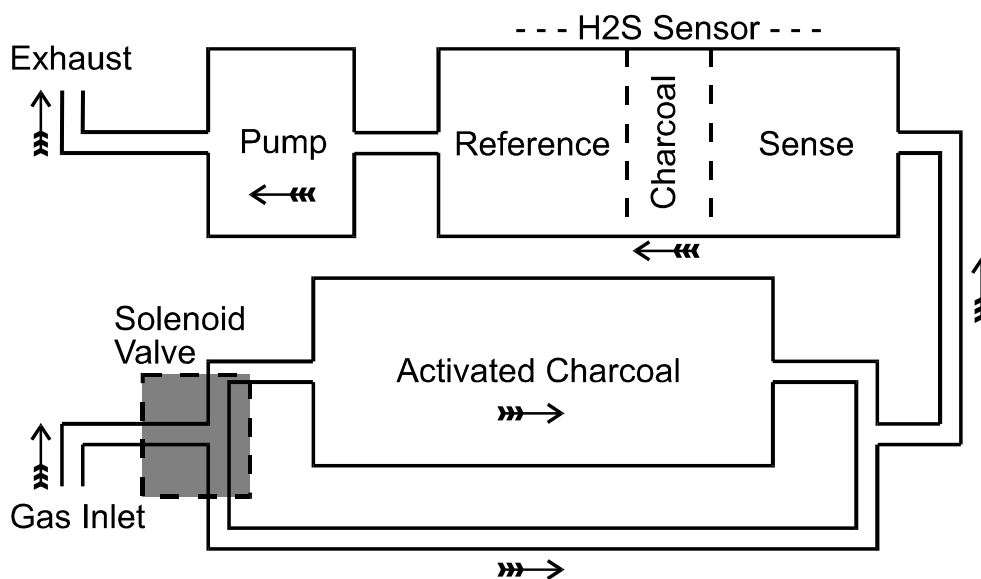


Figure 4.13 Schematic of HSPG Plumbing

Figure 4.13 shows the internal pipework connections of the HSPG for gas flow. The pump is adjacent to the exhaust so that it cannot affect the gas to be sampled. The three-way solenoid valve is on the input. Its orientation with respect to the different flow circuits is important. Solenoid valves only operate reliably at low pressures, if the gas flows across their ports are in specific directions. In this case, the valve also had different sized ports, which affected flow rates, and so the valve was configured so that the most restricted route directed the flow through the sensor. The route having the lower pressure drop was connected to the zero-air filter. This arrangement resulted in flow rates, whether through the sensor alone, or through the sensor and filter, of approximately 0.7 L m^{-1} .

A miniature 12 V diaphragm pump (model PM 11-2, Charles Austen Pumps Ltd, Byfleet, England) was used. Stainless steel tubing, 4 mm ID, was used within the HSPG case, and flexible PTFE tubing externally. All fittings, including the solenoid valve body, were of brass. The sensor and filter housings were built from a combination of acrylic sheet and polycarbonate, embedded in an inert epoxy

compound. The sensor box was sealed using closed-cell, inert EPDM foam rubber strip.

4.2.6 Signal monitoring and logging

The HSPG has a number of data outputs. First, there is the liquid crystal display (LCD). This gives a direct read out, in millivolts, of the output of the differentiator circuitry. No attempt was made to convert these values to H₂S gas concentrations as part of the design, because of the unknown variation in calibration to be expected at the time.

Second, there are two 4 mm sockets on the casing which may be connected to an external datalogger, chart recorder or computer. The sockets receive the same voltage as that for the LCD. The use of these connections can give improved resolution of the HSPG output compared with the built in display.

Finally, the HSPG has a built-in mini-datalogger. This is only an 8-bit logger, however, and its use is therefore mostly limited to instances where H₂S concentrations are in at least tens of ppb because of the poor resolution achieved. In practice each data bit corresponds to approximately 5 ppb. Use of the logger in conjunction with the peak hold circuitry does however enable peak values to be stored within the instrument itself. This is an extremely useful feature as it saves the operator from having to make separate notes of each event.

The peak hold switch permits the viewing of the peak values obtained during a period of field monitoring. If the operator regularly switches between peak and normal display modes, then each peak value can be recorded, either visually from the LCD or by the datalogger, and the peak hold circuit zeroed in readiness for the next peak. Alternatively, the peak hold circuit can be used to record the single highest peak achieved during a measurement period.

4.3 RESULTS AND DISCUSSION

4.3.1 Laboratory trials with the HSPG resistive sensor

The sensor described in section 4.2.1 and shown in Figure 4.1, was used in conjunction with the headstage amplifier described in section 4.2.1. The headstage amplifier output was monitored directly using a chart recorder rather than the complete HSPG circuitry. Using the gas calibration arrangement discussed previously in Chapter 3, the input to the HSPG sensor was switched alternately between the H_2S supply and ambient air.

To avoid risk of overloading the sensor with H_2S , the input was first switched to ambient air. After approximately 5 minutes, the input was switched to the H_2S supply and left until the reading peaked and started to fall. At this point the input was switched back to ambient. This cycle was then repeated at 2-3 minute intervals and with differing values of H_2S . The results of this trial are shown in Figure 4.14.

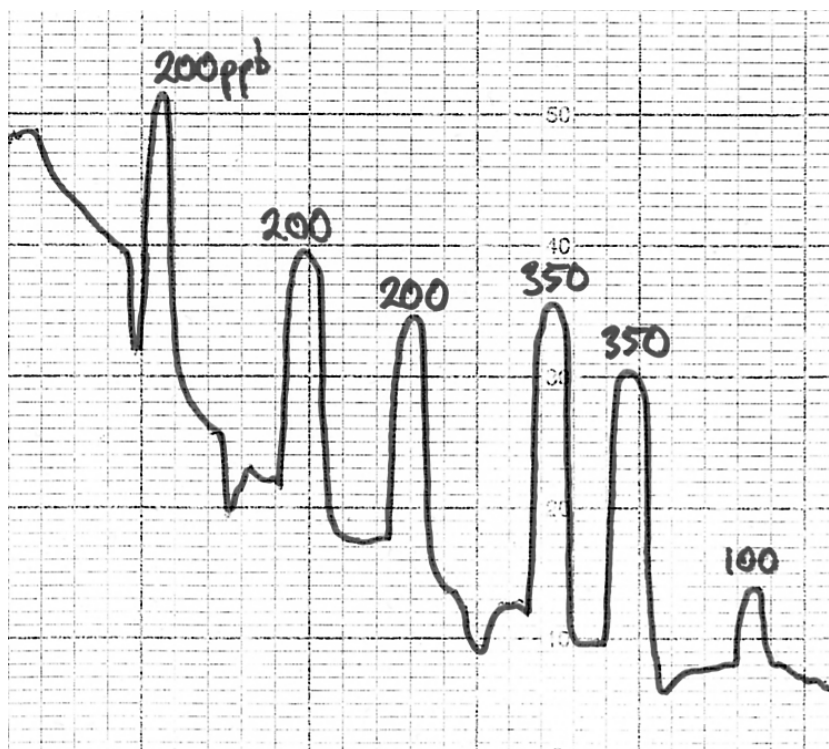


Figure 4.14. HSPG headstage response to H₂S test peaks showing the peak amplitudes on a slowly changing baseline

Although this was a fairly crude technique, the chart recorder output shows peaks whose amplitudes above the baseline are approximately in proportion with the H₂S gas concentration in each case. As can be clearly seen, the baseline decreased rapidly during the experimental period. However, the 200 ppb peaks were almost exactly the same height as each other (40 mm) when the height was measured relative to the average of the 'before' and 'after' baseline heights. The 350 ppb peaks were also of similar height (48 mm) to each other.

The experiment therefore showed that, provided such a mobile baseline could be accommodated, the sensor could be used as a suitable transducer for the monitoring of H₂S.

4.3.2 Field trial with the HSPG headstage

The output of the HSPG headstage was used in a comparison trial with the output of a Jerome 631X portable H₂S analyser (Arizona Instrument Corporation). A laptop computer was used to record the instrument outputs. Both instruments were taken on a short car journey and readings were taken continuously, although not simultaneously. The inputs to both instruments were both taken from the vehicle's cold air ventilation duct - directly from the front grill - to avoid any contamination from gases associated with the vehicle itself.

The readings from the HSPG headstage are shown in Figure 4.15. These show a falling baseline, similar to that in Figure 4.14, on which are superimposed at least three major peaks indicating H₂S incidents. The results from the Jerome 631X are presented in Appendix A (Measurements From Commercial Instruments). Although a direct comparison of readings from the two instruments was not possible, the results obtained in each case show a similar style of a 'background' output, varying within a narrow band, interspersed with much higher, but brief, peaks.

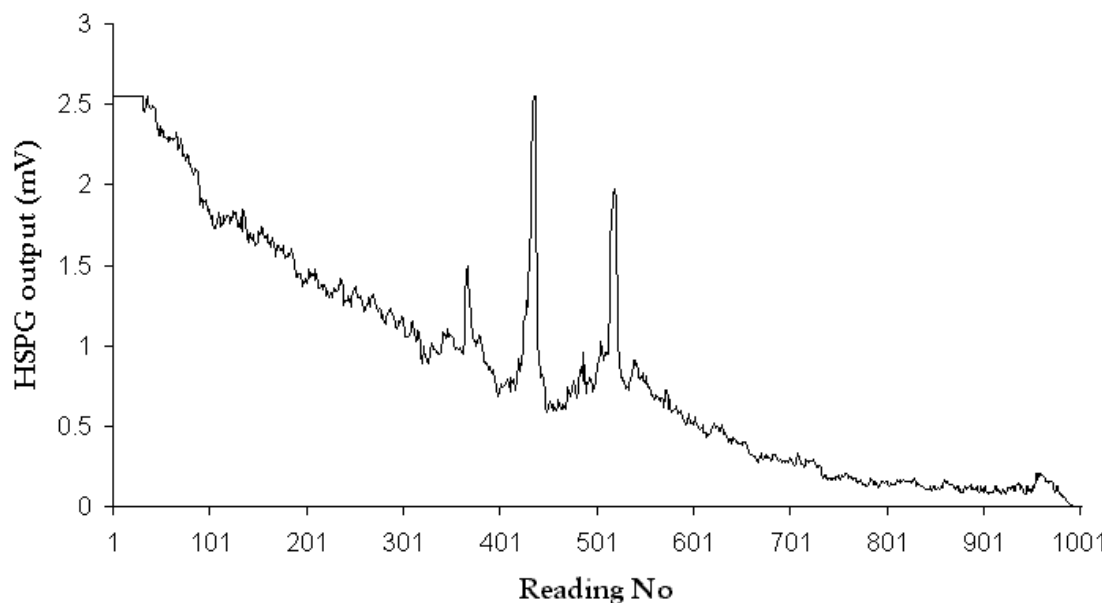


Figure 4.15. Raw data from HSPG sensor.

4.3.3 Calibration and instrument responses

Consistent responses to the following conditions were considered necessary to demonstrate an adequate calibration of the HSPG.

1. An H_2S -free input (ie. a stable baseline for 'zero-air').
2. A step input
(ie. an abrupt increase from zero to a known hydrogen sulphide concentration - taking into account the response time and the response to a continued step value).
3. The descent from a step
(as above; including the response time and the time to stabilise at zero).
4. A step input followed, within less than 1 second, by an equal descent (a 'spike').
5. Repeatability of response to different input concentrations.
6. Linearity

7. Auto-zero mode.

In addition, an understanding was required of any change in response due to:

1. Replacement of sensor gel.
2. Ageing of the sensor gel.
3. Ageing of the activated charcoal in the sensor.
4. Ageing of the activated charcoal in the auto-zero path.

Finally, it was necessary to confirm that the instrument responses were due to genuine voltage changes from the sensor headstage output. Therefore, comparisons were to be made between each of the responses listed above, using the actual sensor, and those from similar signals created artificially, using a millivolt calibrator (Type 1045, Time Electronics Ltd.) instead of the sensor.

A permeation tube calibrator (Model 8550, Monitor Labs Inc. San Diego, U.S.A.) was used in conjunction with one of a series of low output H₂S permeation tubes from Kin-Tek, supplied in the UK by ECO Scientific. Different tubes, employed at different times during the project, ranged in output from 465 to 805 ng min⁻¹, when installed in the calibrator oven at either 40 °C or 50 °C. The HSPG was supplied with either a fraction of the diluted H₂S airstream, or H₂S-free air from the same source as that supplying the calibrator, via manually operated needle valves. A constant flow rate of 0.7 L min⁻¹ was maintained to the HSPG.

4.3.3.1 *Response to H₂S-free air*

The HSPG was designed to respond only to rapid changes in ambient H₂S concentration. It was an inherent aspect of the design, as discussed in section 4.2.3.2, that all slow changes in ambient H₂S concentration would result in an electrical signal which would tend toward zero to provide a stable base line.

Therefore, provided that all changes are within those parameters, the baseline will remain absolutely flat. It is only immediately after occurrences of manual or auto zero that the output will indicate the true ambient H_2S concentration. All other things remaining constant, the indication of this ambient value will then also tend to zero.

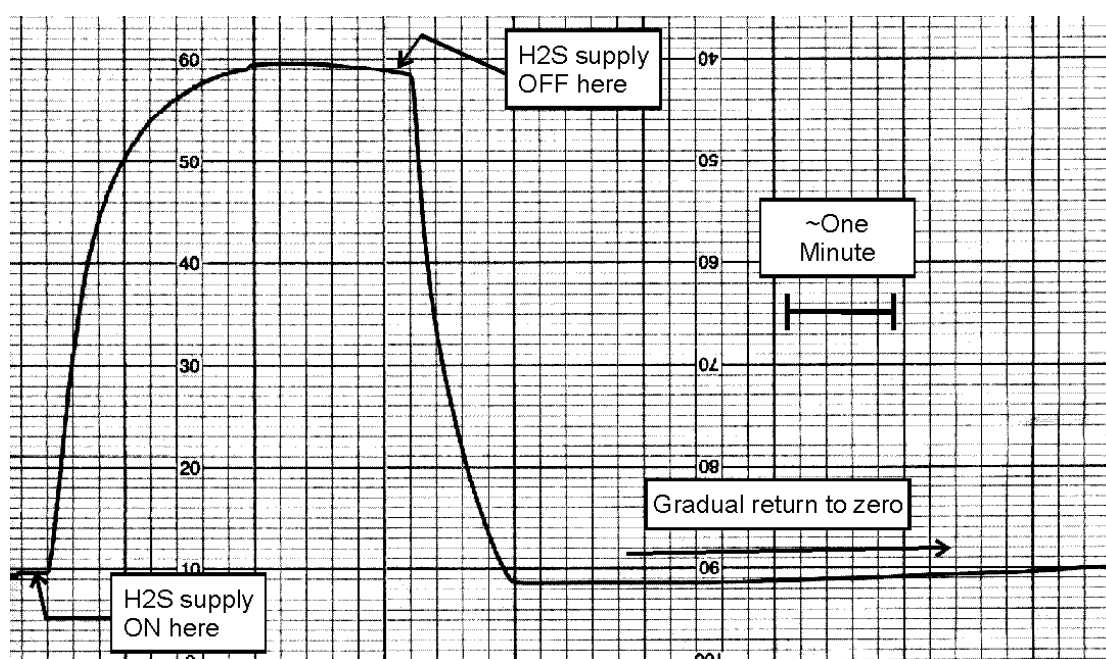


Figure 4.16 HSPG response to step change input of ~ 80 ppb H_2S and subsequent zero air. (Chart speed 20 mm min^{-1} , 2 V fsd .)

4.3.3.2 Response to step changes in input

Figure 4.16 shows a typical response to an abrupt increase in H_2S concentration from zero. It can be seen that the immediate response is extremely rapid (50 % within 15 seconds), but this slows as the maximum height of the 'step' is approached. After reaching a peak, the output decreases slightly as the differentiator input capacitor begins discharging in the manner described in section 4.2. Note, as indicated on the graph, that there is a slight time delay

following the change to and from the H₂S diluted supply. This corresponds to the time required for the gas to travel through the pipework to the HSPG from the needle valves.

After a return to zero-air, the output voltage initially changes rapidly and then slows. This time however, the output voltage passes through zero and becomes slightly negative before gradually returning to zero as also described in section 4.2.

The equivalent response in the voltage simulation shown in Figure 4.17 is far sharper. There are a number of possible reasons for this discrepancy. Firstly, in the gas calibration, the changeover to H₂S from zero-air is not instantaneous - due to a combination of initial mixing and the operating time for the needle valves. Secondly, the reaction of the new gas with the sensor gel coating must take a finite time, and will only reach equilibrium when the rates of H₂S adsorption and desorption are equal - due to the nature of the reversible reaction taking place in the gel. The simulated response suffers from none of these delays.

Note: To emphasise the characteristics of the curves in the simulated responses, it was necessary to alter the value of the differentiator capacitor, and therefore the time scale of the chart recording.

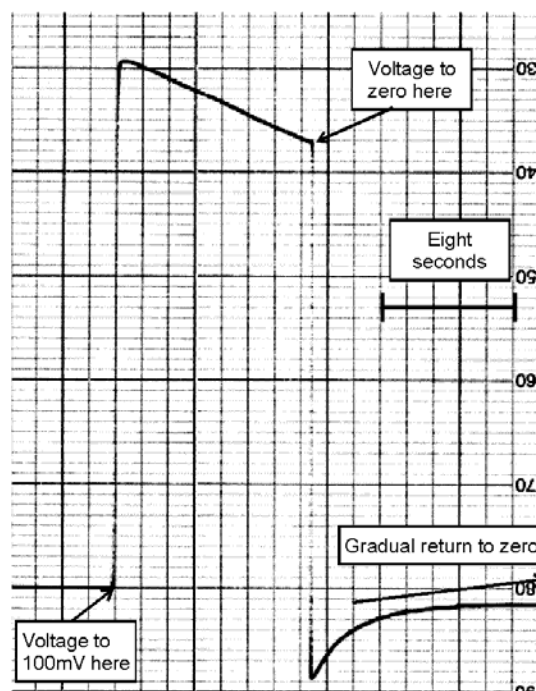


Figure 4.17. HSPG response to voltage input simulating step input of H_2S and return to zero. (Chart speed 200 mm min^{-1} , 200 mV fsd.)

After reaching a maximum, the voltage falls steadily due to capacitor discharge - as occurs with the sensor. When the input voltage returns to zero, the output would attempt to fall by an identical amount to the initial rise, but negative voltage excursions are largely prevented by the action of the germanium diode previously described, and the output gradually returns to zero volts as before.

The foregoing describes the HSPG responses to single steps, such as those used for calibration purposes, but it is also necessary to consider the responses if the initial step is followed by one or more subsequent steps, or spikes - for example those which might be encountered in a roadside environment.

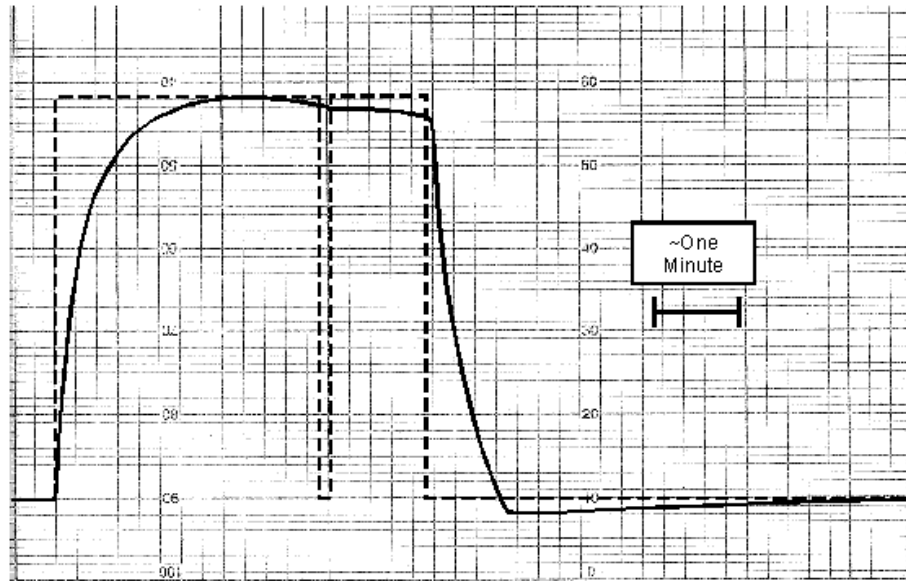


Figure 4.18 Effect on HSPG response of two overlapping stepped peaks of equal H_2S concentration. Dotted line indicates 'perfect' response.

Figure 4.18 shows the effect on the HSPG response of two overlapping steps, up and down, of nominally identical concentrations in the sensor. The second step occurs before the first step has had the opportunity to return to zero but after the voltage has started to fall slightly. The second maximum is slightly lower than the first because the differentiator input capacitor voltage will have drooped slightly.

If the second peak occurred after the first had returned to, and passed through, zero - ie before the baseline was fully recovered and therefore the signal was still negative - then the second peak would be similarly reduced in amplitude - but of equal height from base to peak. In either of the above cases, the reduced amplitude of the second maximum would still be within the $\pm 10\%$ specified in the HSPG design.

It is important to note however, that the height of the second maximum, in the case of the two peaks which overlap, could be higher or lower than the second

peak in the case where the second peak falls in the area of the first peaks 'zero depression'. As discussed previously, the reduction of peak height in the latter is limited by the forward voltage of the germanium diode, whereas in the former, it is only affected by the extent of capacitor voltage droop.

Because of the almost instantaneous response of the HSPG, to a voltage simulating the sensor, it is not possible to adequately demonstrate the effect of two overlapping 'concentrations'. These are always revealed as two distinct steps - as seen in Figure 4.19. The same figure does however show the effect of the zero depression following a broad step and confirms that the second step height, if not its amplitude, relative to the 5 V bias voltage, is identical to the other.

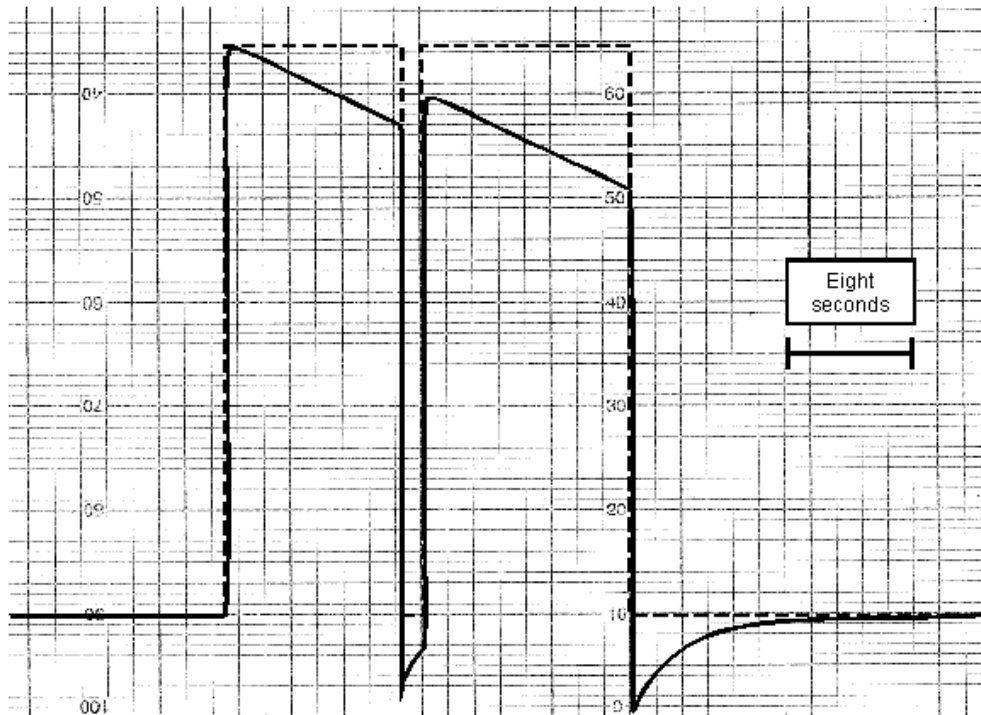


Figure 4.19 Simulation of HSPG response to two closely following peaks of H_2S gas concentration. Dotted line indicates 'perfect' response.

The auto-zero mode causes the HSPG to behave in a similar manner to that where a downward step change in H_2S concentration occurs. At the end of the auto-zero period, the HSPG responds as it would when being presented with the ambient

concentration as another upward step change.

4.3.3.3 *Ageing of gel and carbon filters*

It was found that the sensor gel, after the initial evaporation of the carrying solvents, gave consistent results for up to ten days. During the first 24 hours, the electrical output appeared somewhat noisy ($\pm 20\%$), presumably due to residual solvents or other chemical instability after mixing, and so the HSPG was not used during this period. Daily calibrations were then performed, but it was found that these did not vary significantly until approximately the tenth day, after which the sensitivity fell at approximately 10 % per day. It was suspected that this was due to drying of the gel coating.

The lifespan of the carbon granules, in both the reference chamber and in the zeroing chamber, is dependant upon the total H_2S dose to which they are each subjected. Because the HSPG was used in various ways, and calibrated under differing regimes, at different times, it proved difficult to estimate how soon the carbon would become unusable. The prime symptoms of carbon exhaustion were loss of sensitivity and inability to zero the HSPG. The maximum period of use, achieved without changing the carbon in either chamber, was approximately one month. However, it was decided that, as carbon replacement and gel refreshment each entailed undoing the measurement cell, both activities should be done every ten days.

4.3.3.4 *Repeatability of response to different input concentrations*

The calibration curve for the HSPG is shown in Figure 4.20. The formula for the curve was calculated using the Excel ‘solver’ function. This curve is a composite produced from a number of different experiments using varied H_2S gas

concentrations on different days and with sensor gels of different ages. Viewed separately, each day's calibration produced a curve of similar shape to Figure 4.20. All the points on the curves obtained however, fell within $\pm 10\%$ of the values indicated in the composite curve. This close repeatability was very useful in quickly estimating H_2S concentrations during experiments.

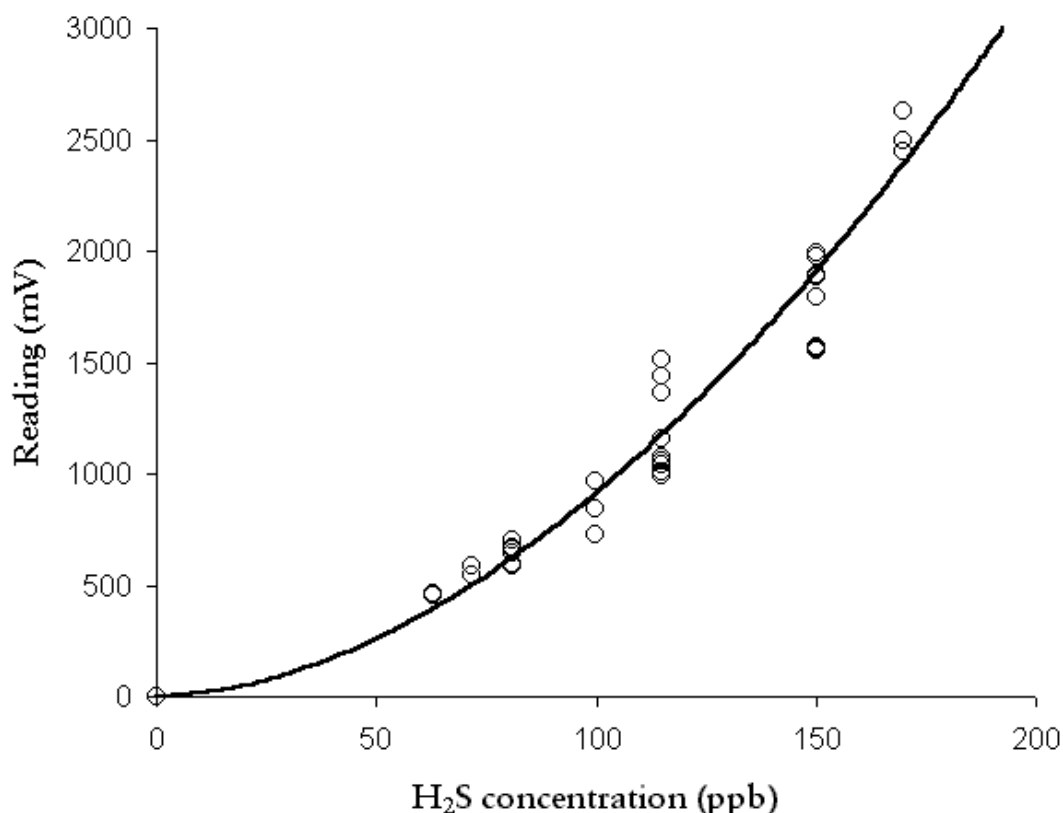


Figure 4.20 HSPG calibration curve. Curve formula is $C = 2.3E^{0.5508}$ (where $C = \text{H}_2\text{S}$ concentration in ppb and $E = \text{HSPG}$ reading in millivolts)

4.3.3.5 Linearity of HSPG response

Figure 4.20 shows that the HSPG does not have a linear response. This was also suggested earlier by Figure 4.14, in that the 100 ppb peak was noticeably less in magnitude than half that of the 200 ppb peaks.

Therefore, it now seems likely that the complete response curve for the sensor is

sigmoidal in character. This would be in agreement with the responses of other gels to chemical and biological agents.

4.3.4 HSPG limitations

The HSPG is not suitable for the continuous monitoring of 100 ppb H_2S or greater, as the activated charcoal employed will rapidly become exhausted. However, this was not the intention of this design, for which a proprietary digitally based instrument (such as the Jerome 631X previously described) would be more appropriate.

A slow change in concentration of H_2S , such as small changes in ambient concentration, would not be detected if this was similar in magnitude to the rate of charging or discharging of the differentiator capacitor. However, these would become measurable after each zero setting procedure.

The need to regenerate the sensor gel coating approximately every ten days is an inconvenience and could interrupt a series of experiments. There is also the need to wait another day after regeneration, until the sensor coating has stabilised, before use.

4.4 SUMMARY

The hydrogen sulphide peak gauge (HSPG), has been shown to respond extremely rapidly to changes in H_2S concentration and to reveal the nature of variations in concentration more accurately than any other known portable instrument. To some extent because of this, the calibration of the HSPG proved difficult. It is evident from field experiments that the HSPG is capable of much more rapid response than the changes the gas calibrator was able to provide, because plumbing

volume, flow rate and switching valve constraints meant that step changes in calibrator output were inherently impossible.

It is acknowledged that for a commercial instrument, a sensor that does not require weekly replacement or daily calibration is an essential pre-requisite. Therefore, metallic oxide sensors should be considered where the technology is available for their production.

Chapter 5: FIELD EXPERIMENTS

This chapter is divided into two sections. The first section (5.1) outlines those experiments which relate to the development of the DRs, described in Chapter 3, and their use for the measurement of long term measurements. The second section (5.2) outlines experiments conducted using the HSPG, described in Chapter 4, for the measurements of peaks.

Each site used, and the criteria for its selection, is described in the appropriate experimental section the first time the site is referred to.

5.1 LONG TERM MEASUREMENTS

5.1.1 Experiment 1: ACUs at Molehill Farm

The objective of this experiment was to determine whether the aspirated collection units (ACUs) described in section 3.2, were a viable method of monitoring ambient H_2S .

A site was chosen close to junction 24 of the M1 motorway, for the following reasons:-

- It is close to the laboratory used for sample preparation and analysis.
- Two heavily used major roads, totalling 12 lanes, run alongside each other in this vicinity. Likely concentrations of H_2S were not known at this stage therefore the large amount of traffic would maximise the chances of H_2S detection.
- The motorway is in a cutting in this locality. When the wind is in the prevailing (south westerly) direction, the overbridge tends to direct traffic fumes from both roads towards the eastern sampling point. This was expected to maximise any differential in H_2S concentrations between the two sites.

- The farmer at Molehill Farm was agreeable to the use of his land for this work.

Two ACUs were deployed adjacent to Molehill Farm in the locations indicated by X and Y in the site layout (Figure 5.1).

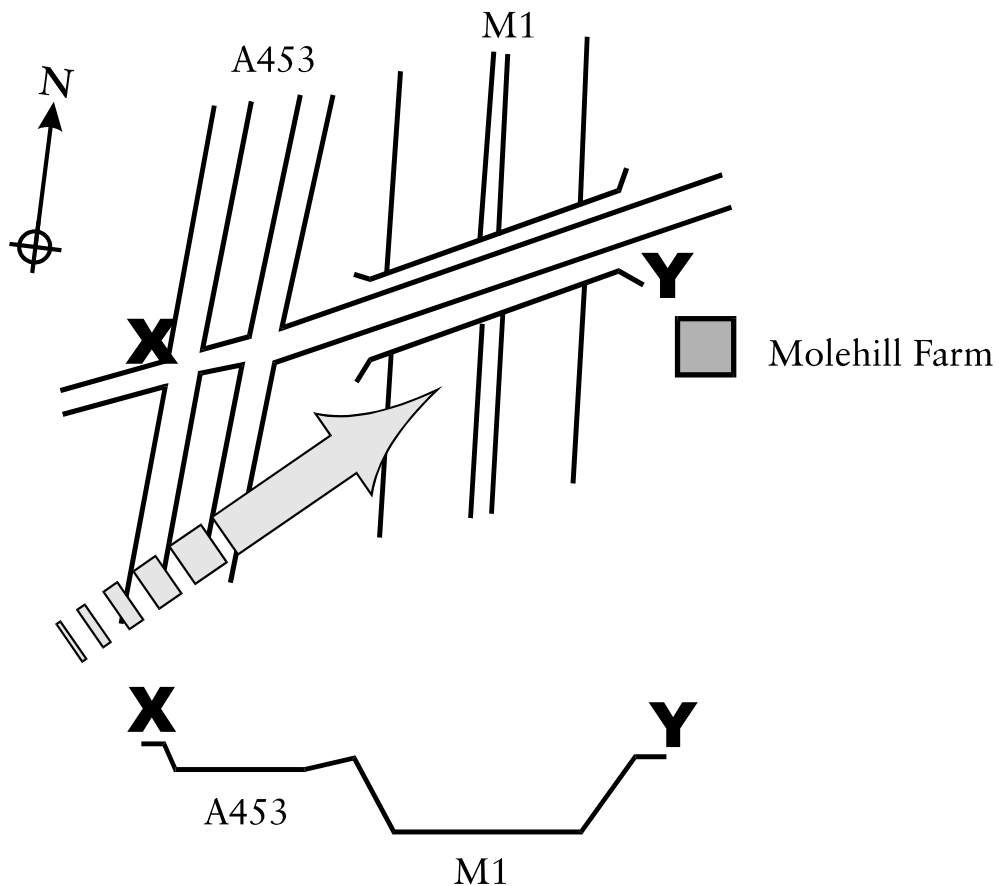


Figure 5.1. Site plan of Molehill Farm showing direction of prevailing wind and cross section between west and east sites.

The view westwards from the farm entrance is shown in Figure 5.2. The western ACU was situated at the foot of the distant hedge on the extreme right of the photograph. Therefore, with the wind from the direction shown, only the eastern ACU was in the path of vehicular pollution.



Figure 5.2. View from Molehill Farm, westwards over M1 to A453.

The absorbing solution used was as described in the ISC method (American Public Health Association Intersociety Committee, 1977) and not the formulation described in section 3.2.3 which had not yet been developed. The ACUs were exposed for 3 hours 30 minutes. The weather was warm but damp throughout the exposure period. The temperature varied between approximately 26 °C and 21 °C whilst the humidity varied between 48 % and 66 %.

The results of this experiment are shown in Figure 5.3. Each absorbance was measured against a de-ionised water blank. All subsequent experiments used blanks which were unexposed solution which was otherwise subjected to the same environment as the measurement samples. The stacked bar charts indicate the amounts of sulphide captured in each of the series bottles. At this stage the absolute values of sulphide could not be calculated, nor converted into average concentrations over the exposure period. This was because the presence of sulphide in the third bottle, from each ACU, indicated that not all available sulphide might have been captured and therefore that calculated concentrations

could be inaccurate.

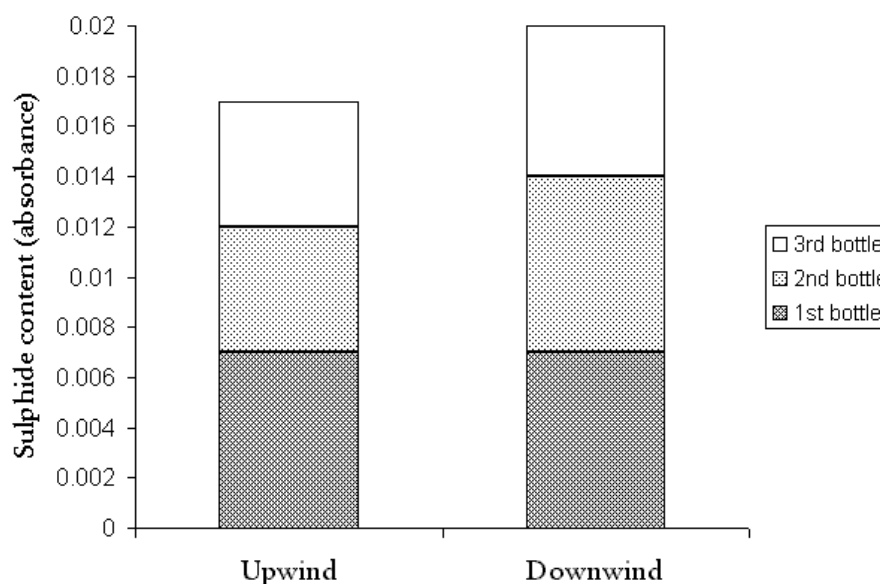


Figure 5.3. Relative absorbances due to sulphide captured upwind and downwind of M1 motorway and A453 dual carriageway.

5.1.2 Experiment 2: ACUs at Molehill Farm

The objective, and procedure, for this experiment was the same as that described in section 5.1.1 (Experiment 1), except that the sample boxes were exposed for 6 hours and 30 minutes to try and obtain a larger distinction in the results between the upwind and downwind sites. The dreschel bottles, in this and subsequent ACU experiments, were fitted with the perforated plastic caps described in section 3.2 to reduce the size of the bubbles produced. The weather was cold and damp. The temperature fell from approximately 14 °C to 5 °C and the humidity rose from approximately 42 % to 73 % during the sampling period. The results for this experiment are shown in Figure 5.4.

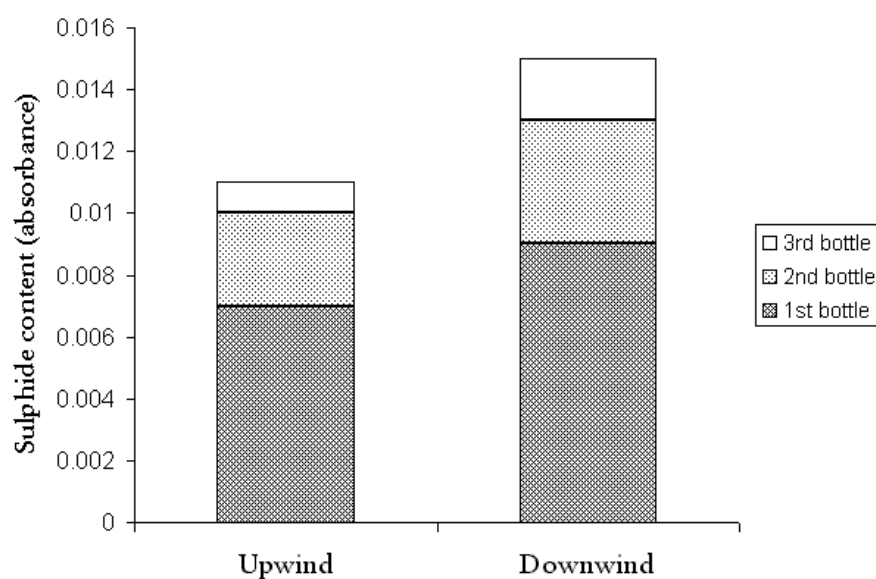


Figure 5.4. Relative absorbances due to sulphide captured upwind and downwind of M1 motorway and A453 dual carriageway.

5.1.3 Experiment 3: ACUs at Molehill Farm

The objective, and procedure, for this experiment was the same as Experiments 1 and 2, described in sections 5.1.1 and 5.1.2, except that the sampling period was increased to 54 hours to try and increase still further the distinction between the measurements from the upwind and downwind sites. The weather was again cold and damp with temperatures falling from approximately 10 °C to 5 °C, and humidity approaching 100 % throughout the sampling period. The results for this experiment are shown in Figure 5.5.

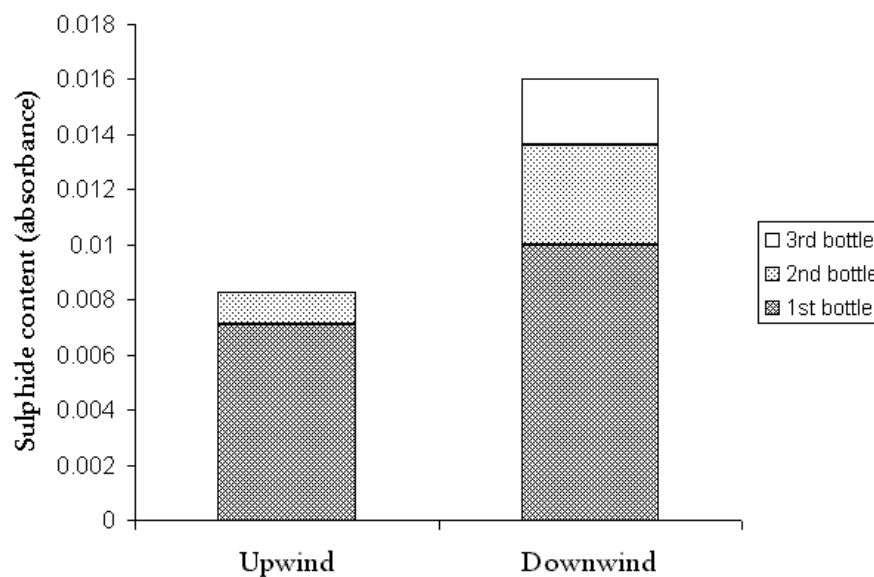


Figure 5.5. Relative absorbances due to sulphide captured upwind and downwind of M1 motorway and A453 dual carriageway.

5.1.4 Experiment 4: ACUs at Molehill Farm

This experiment was similar to that described in section 5.1.3 above except the sampling period was for 26 hours and the collection solution used in the dreschel bottles was the new formulation described in section 3.2.3 (Deuchar *et al.*, 2002). The objective of the experiment was to test whether the new solution gave improved results over its predecessor. The new formulation for the collecting solution is referred to hereafter as ‘DR solution’. The weather was again cold and damp with temperatures of only a few degrees Celsius. The results of this experiment are shown in Figure 5.6. The total of the absorbances obtained, upwind and downwind of the motorway, were later translated into atmospheric concentrations of H_2S of approximately 2 ppb and 4 ppb, respectively.

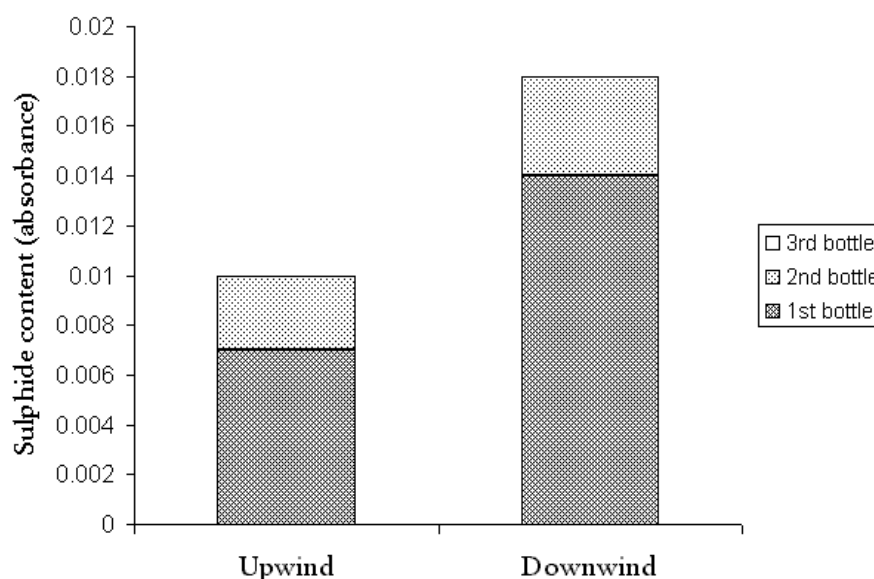


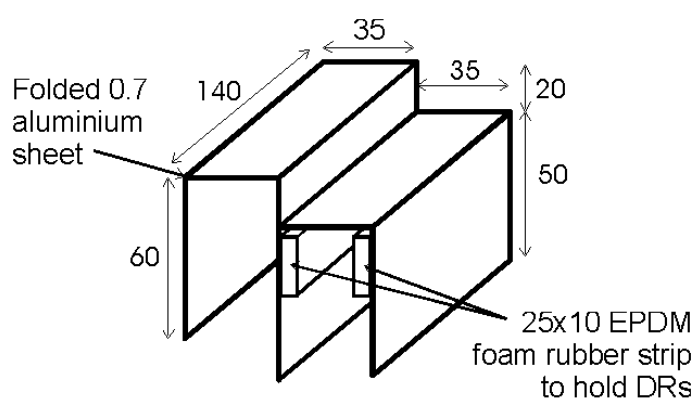
Figure 5.6. Relative absorbances due to sulphide captured upwind and downwind of M1 motorway and A453 dual carriageway.

5.1.5 Experiment 5: DR exposure at five sites

The object of this experiment was to test the newly developed passive technique, described in Chapter 3, section 3.2.5. Single diffusion reservoirs containing 7 mL of DR solution were fixed to fences at five local sites approximately 0.8 m above the ground surface. The sites were adjacent to one of the University fields at Sutton Bonington (denoted F12), alongside, and east of, the M1 motorway at Long Whatton (LWE), either side the M1 motorway near Molehill Farm (J24W & J24E), and adjacent to Kegworth water treatment works (KWT).

The sites used in addition to the previously described Molehill Farm locations were chosen for the following reasons. The F12 site was chosen because of its completely rural location and proximity to the laboratory. The LWE site was used because it, like J24E, was downwind of the motorway but in an otherwise rural location with no other major road nearby and the KWT was chosen because it was expected that the treatment works would be a considerable source of H_2S .

Extra DRs were fitted with blank caps, for use as assay blanks. The DRs were transported to the measurement site in sealed plastic boxes with the caps and membranes upwards. The DRs were then fitted into purpose made holders, to the specification in Figure 5.7. The holders were clipped on a convenient fence rail, with the membranes in the downward position to be in contact with the DR solution. The DRs were exposed for 24 hours and were deployed and collected in the same order. Therefore, although the period of measurement was the same for each DR, the individual sampling periods were staggered by up to 15 minutes.



All dimensions in mm

Figure 5.7 Fence holder for up to three DRs

After retrieval, the DRs were transported back to the laboratory, membranes upward but covered by a thin plastic sheet, in the same sealed, plastic boxes and refrigerated until analysis the following day. The wind direction was from the south-west throughout the experimental period.

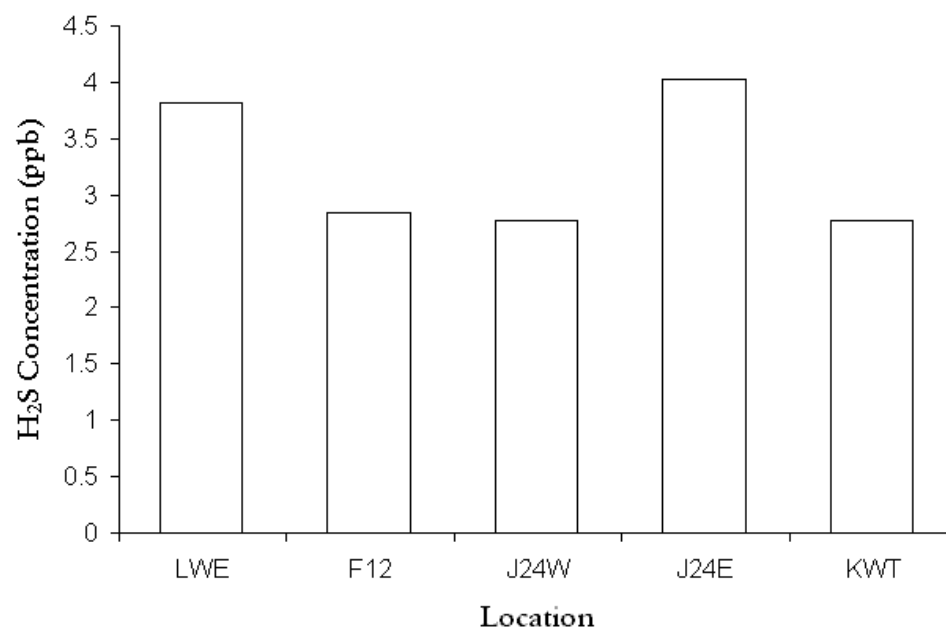


Figure 5.8. H₂S concentrations at various roadside and rural locations

The results of this experiment are shown in Figure 5.8. The calibration was carried out as described in section 3.2.

5.1.6 Experiment 6: DR exposure at two sites

This experiment was carried out in a similar manner to that described in Experiment 5, section 5.1.5 but the DRs were set out with three replicates at each of two different sites for a period of 11 hours. One site was at Trent Lock, Sawley, South Derbyshire (TL), at a rural, traffic free, riverside location and the other was adjacent to, and downwind of, the M1 motorway at Watford Gap (WG), Northamptonshire, in an otherwise rural location. A further three DRs were kept unexposed in the laboratory for use as blanks. The objective was to assess the variability between replicates at each site.

The results of this experiment are shown in figure 5.9.

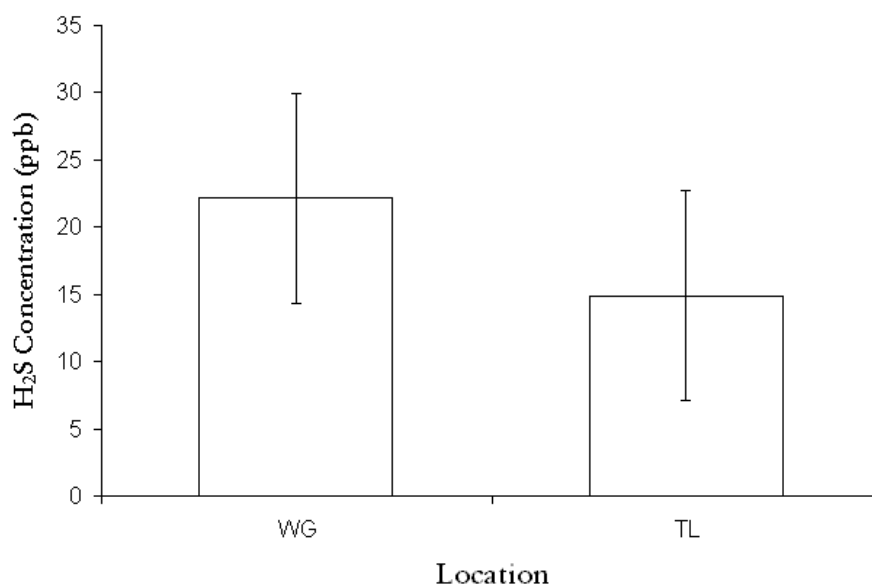


Figure 5.9. H₂S concentrations adjacent to a motorway (WG) and at a rural location (TL)

5.1.7 Experiment 7: DR exposure at a single site

This experiment was carried out in a similar manner to that described in Experiment 6, section 5.1.6 but the DRs were set out with three replicates each at Normanton on Soar, Nottinghamshire (NoS) for ten days - a rural, riverside site. A further three DRs were kept unexposed in the laboratory as controls. The objective was to further investigate typical rural H₂S concentrations at a different site and assess the variability of replicates.

The results of this experiment are shown in Figure 5.10.

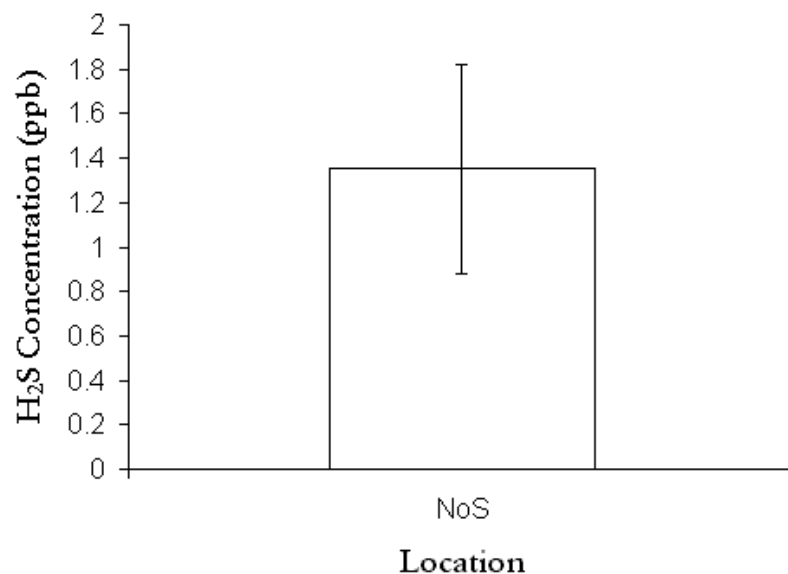


Figure 5.10. H₂S concentrations at a single rural location

5.1.8 Experiment 8: DR exposure at three sites

This experiment was carried out in a similar manner to that described in Experiment 7, section 5.1.7 but the DRs were set out with three replicates at each of three different sites for 3 days. The sites were F12, Long Whatton west of the M1 motorway (LWW) and Long Whatton east of the M1 motorway (LWE). A further three DRs were kept unexposed in the laboratory for use as controls. The objectives were to make further comparisons between the ambient H₂S recorded at each site over the same time period and also to compare ambient H₂S on both upwind and downwind sides of a major road. The wind direction was from the east throughout the experimental period.

The results of this experiment are shown in Figure 5.11.

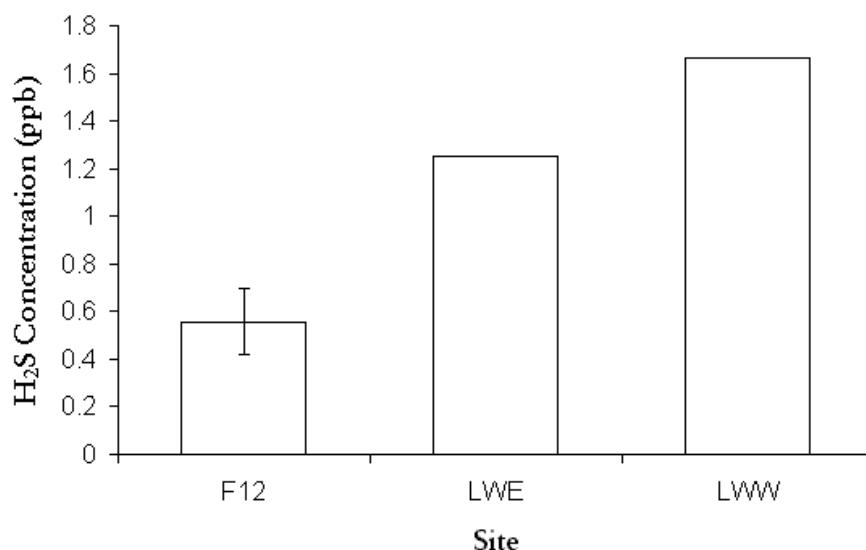


Figure 5.11. H₂S concentrations at various locations including east (upwind) and west (downwind) of a major road

5.1.9 Experiment 9: DR exposure at three sites

This experiment was carried out in a similar manner to that described in Experiment 8, section 5.1.8. The DRs were set out with three replicates at the same three sites for a period of seven days. A further three DRs were kept unexposed in the laboratory for use as controls. The object was to repeat the previous experiment but over a different sequence of days and to compare the two sets of results and see whether responses were consistent. The wind direction was from the south-west throughout the experimental period.

The results of this experiment are shown in Figure 5.12.

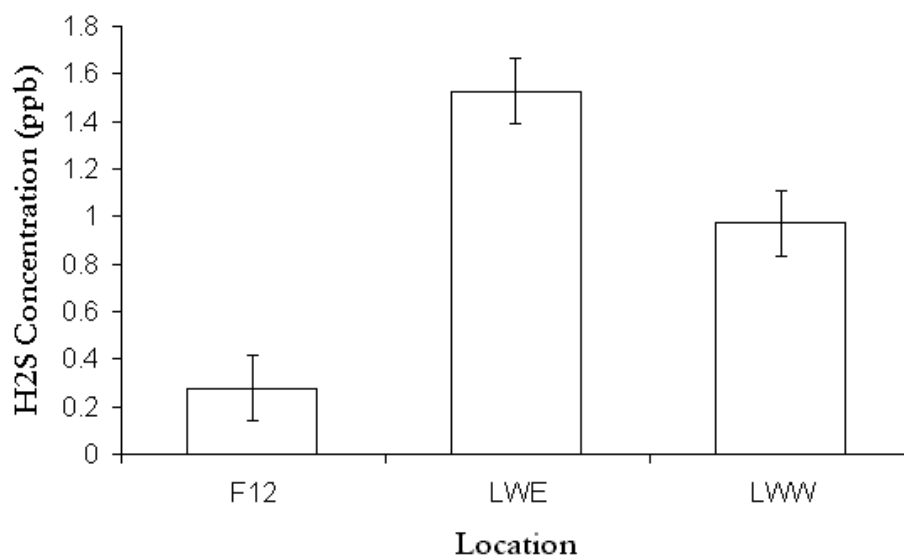


Figure 5.12 H₂S concentrations at various locations including west and east of a major road

5.1.10 Experiment 10: DR exposure at five sites

This experiment was carried out in a similar manner to that described in Experiment 9, section 5.1.9. The DRs were set out with three replicates at each of five different sites (including the three from the previous experiment) for a period of 24 hours. The additional sites were Molehill Farm, between the A453 dual carriageway and the M1 motorway (MHM), and KWT. A further three DRs were kept unexposed in the laboratory for use as colorimeter blanks. The objective was to further investigate the variability of ambient H₂S simultaneously at different sites. The wind direction was from the south-west throughout the experimental period. This meant that the location LWE was downwind of the motorway, MHFM was downwind of the A453 dual carriageway and KWT was downwind of Kegworth water treatment works.

The results of this experiment are shown in Figure 5.13.

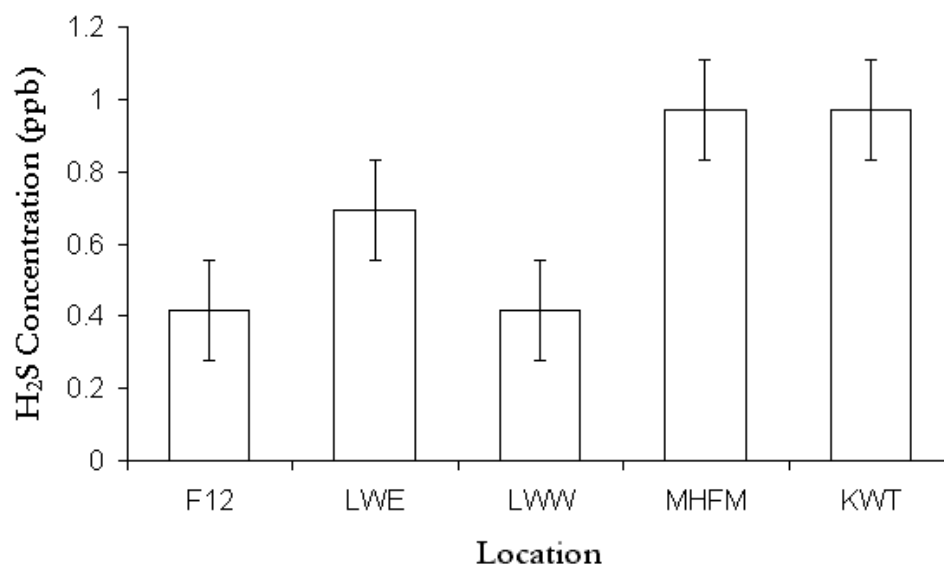


Figure 5.13 H₂S concentrations at various locations including west and east of major roads

5.1.11 Experiment 11: DR exposure at six sites

This experiment was carried out in a similar manner to that described in Experiment 10, section 5.1.10. The DRs were set out with three replicates at each of six different sites (including the five from the previous experiment) for a period of five days. The additional site used was MHW. A further three DRs were kept unexposed in the laboratory for use as colorimeter blanks. The objective was to repeat the previous experiment for a longer time period to assess long term variability of H₂S concentrations in the atmosphere. The wind direction was from the east throughout the experimental period. This meant that the location LWW was downwind of the motorway. MHFM was upwind of the A453 dual carriageway, but downwind of the M1 motorway. MHFW was downwind of both the motorway and the dual carriageway and KWT was upwind of the water treatment works.

The results of this experiment are shown in Figure 5.14.

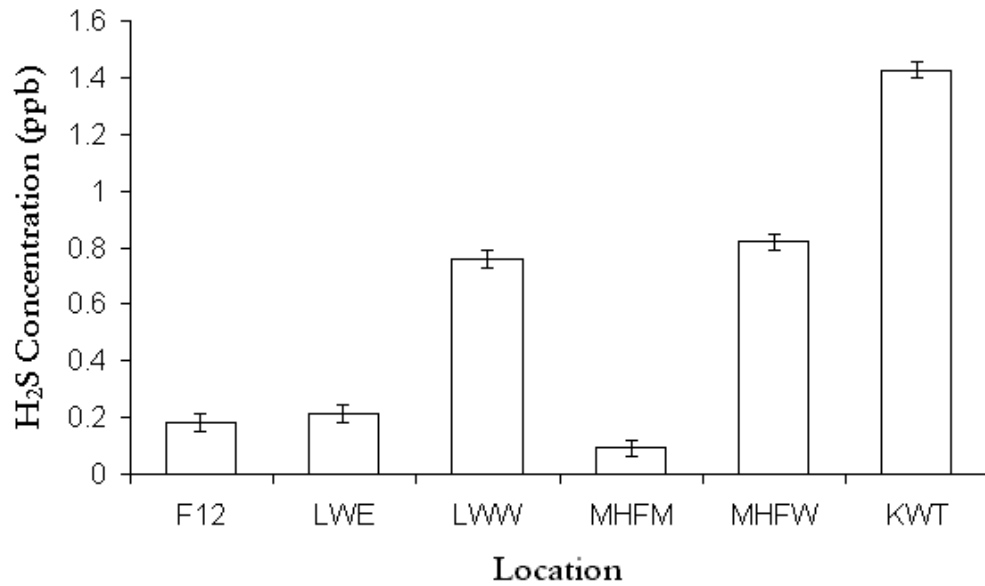


Figure 5.14. H₂S concentrations at various locations including west and east of major roads

5.1.12 Experiment 12: DR exposure on part of a land fill site

This was a preliminary experiment with the objective of assessing the suitability of DRs for the monitoring of H₂S around a landfill site. For the monitoring of landfill H₂S, the survey method employed may vary according to requirements. For example, a grid formation over the entire site may be used to determine spatial variation or a perimeter survey employed to assess the significance of gas migration from the site.

The particular site surveyed had a history of nuisance odours which were attributed to H₂S by the site owners. The study site was first used for landfill over 20 years ago and was progressively covered with a mixture of soil and quarry waste until completion some 10 years ago. H₂S originates from plasterboard, or other gypsum waste, buried with organic material, because of reaction with acidified leachate. A variety of trees was planted on completion of the covering. The site was approximately 300 m square. The whole site was traversed first on foot and areas identified where the smell of H₂S seemed particularly strong.

A cover-box technique, employing four DRs, was used on one portion of bare earth where the smell of H_2S was evident in the south-west corner of the site. Two other DRs were taped to a post, approximately 0.8 m above ground, adjacent to the cover box. Two more DRs were taped to another post near a leaking gas valve in the south-eastern corner of the site, approximately 140 m from the cover boxes, and a further two to a third post midway between the two locations. The DRs were fixed in the inverted position so that the membranes faced downward and were in contact with the absorbing solution. Additional DRs were kept unexposed for use as controls. Heavy duty, silver, self-adhesive tape was used to protect the DRs from direct sunlight and minimise solar heating. The DR blanks were similarly taped to an additional post. All samples were exposed for four hours except for two of the four associated with the cover box, which were only exposed for the first two hours.

The results of this experiment appear in Figure 5.15.

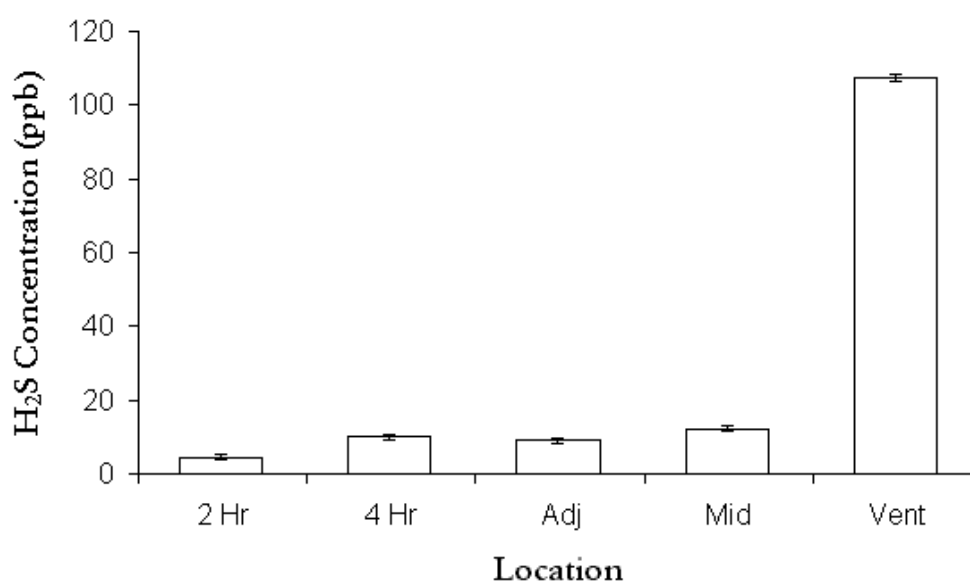


Figure 5.15. H_2S concentrations on a landfill site. 2 Hr and 4 Hr are timed cover box measurements. 'Adj', 'Vent' and 'Mid' are 4 hour DR measurements made adjacent to the cover box, the eastern vent and midway between these points, respectively. Non-cover box measurements were made on posts 0.8 m above ground.

5.1.13 Experiment 13: DR area survey on a landfill site

The object of this experiment was to map typical H_2S concentrations around one of the H_2S 'hot-spots' identified on the landfill site described in section 5.1.12. Posts (W1-W4, X1-X4, Y1-Y4 and Z1-Z4) were driven into the ground around the leaking valve on a 4x4 matrix with an interval of 7 m between posts as indicated in Figure 5.16. The posts were set out so that the gas valve coincided with post B2. Two additional posts were driven into the ground adjacent to the valve so that sampling of the immediate environment at the valve could be made in 1209 sectors. The asymmetrical nature of the grid layout assumed a longer 'plume' of H_2S would be evident to the north east due to the prevailing south westerly wind.

Single DRs were taped to each post 0.8 m above the surface of the ground. The results of this experiment appear in Figure 5.16. The DR measurements were mapped using Golden Software's 'Surfer' package, version 7, and interpolation performed by kriging.

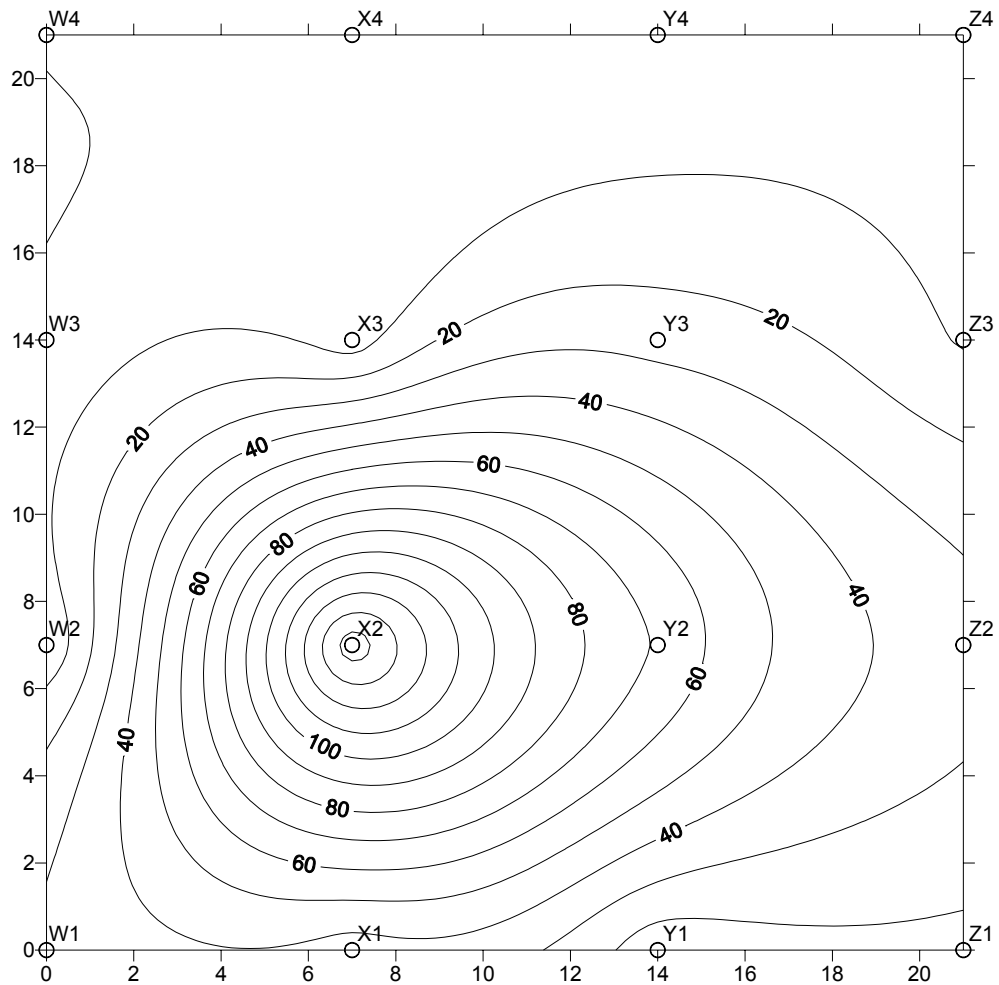


Figure 5.16. H_2S concentrations around a leaking landfill gas valve (X2). Distances in metres, contours show ppb H_2S .

5.1.14 Experiment 14: DR whole site survey of a landfill site

A whole-site survey was conducted of the landfill site described previously in section 5.1.12, with the objective of refining the location of hot-spots. The site was set out with posts at each intersection of a 50 m grid. A single DR was fixed to each post. The post layout and results are shown in Figure 5.17.

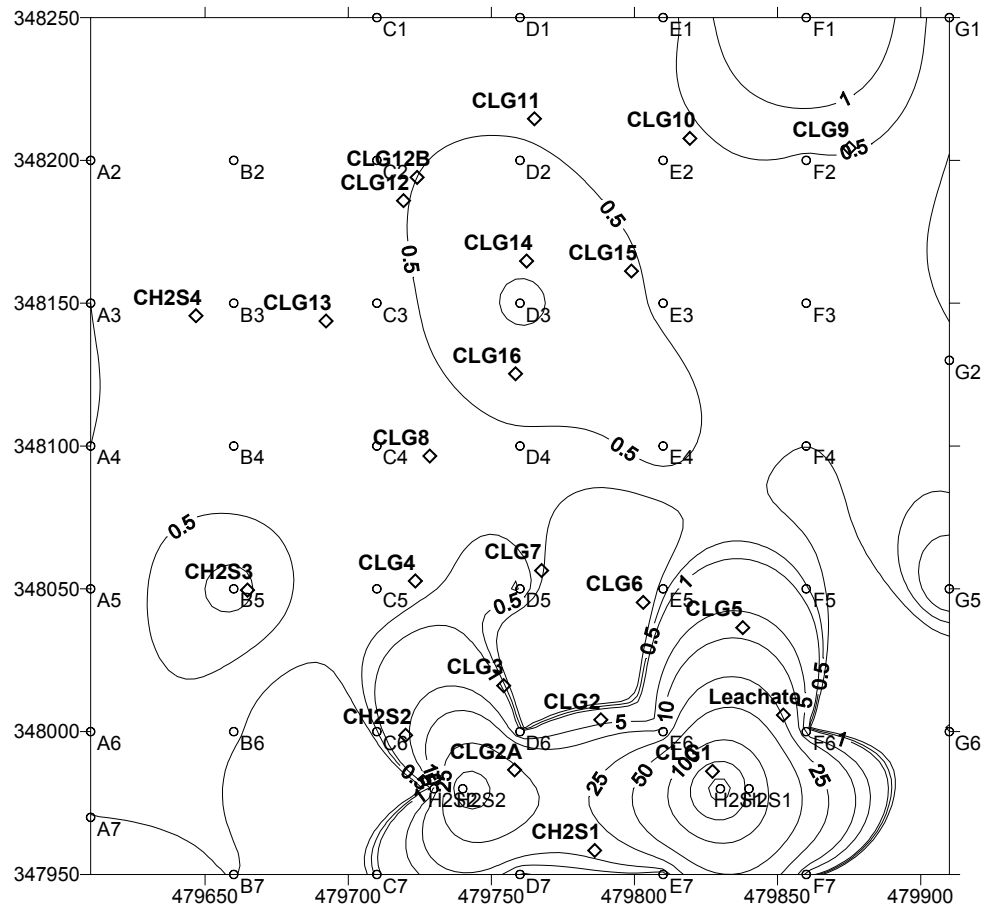


Figure 5.17. Landfill site survey using DRs. Eastings and northings in metres, contours show ppb H_2S .

5.1.15 Experiment 15: DRs on a detail survey of a landfill site

Experiment 14 (section 5.1.14) revealed that nearly all H_2S emissions originated from one part of the site. Therefore, this experiment related only to the south eastern quarter of the site, some 150 m square, which was identified as the predominant area for H_2S emissions. The topography of the selected area is shown in Figure 18, along with the positions of the relevant sampling posts (A1...A4, B1...B4, C1...C4, D1...D3 and CH2S1) and gas valves. The valve CH2S1 is the prime source for H_2S emissions, whereas the valves CLG2 and CLG3, and the leachate well, are secondary sources.

Sufficient vials were prepared to allow three DR replicates at each of the 16 monitoring locations, plus three additional DRs for use as unexposed assay blanks. Aliquots of 7 mL of the absorbing solution were placed in each vial. Three vials were fitted with plain caps to be used as the blanks and the remainder fitted with a perforated cap and membrane.

The DRs were taped to the posts, with the membranes exposed downwards, 0.8 m above the ground surface. The time was noted at which the first and last DRs were set out.

Meteorological data was not recorded on site, but temperatures, wind speed and wind direction were monitored hourly throughout the exposure period at a site a few miles away. These data were supported by qualitative observations on site. Previous experience had shown that the only notable meteorological differences between the two sites were in the timing of events. No rainfall was recorded during the sample period.

After 50 hours, at the end of the exposure period, the DRs were recovered in the same order as that in which they had been set out, and the start and finish times were again noted.

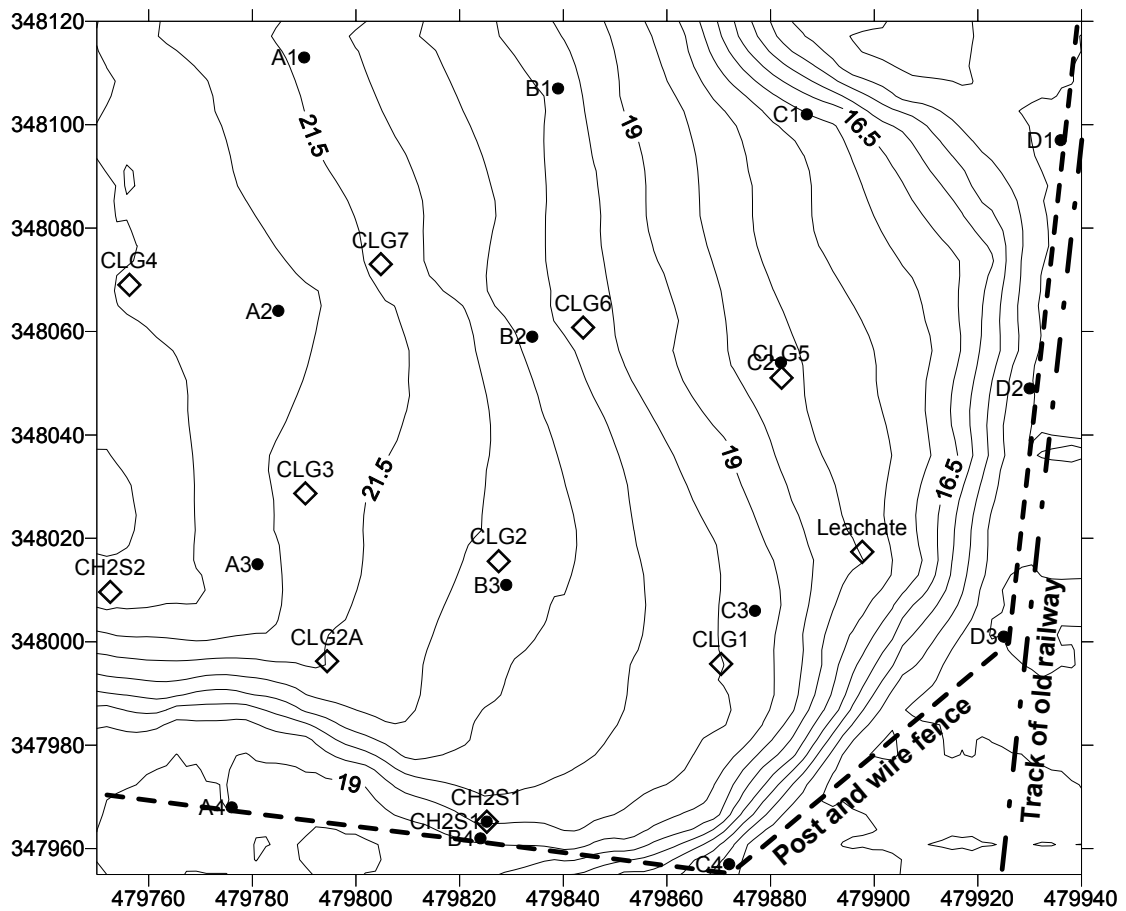


Figure 5.18. Topography and gas valves around a landfill site. (All dimensions in metres. Heights are above mean sea level.)

During the exposure of the DRs, the HSPG was also used to take instantaneous readings at each monitoring point. This is further described in Section 5.2.5. The results of the DR spatial survey are shown in Figure 5.19.

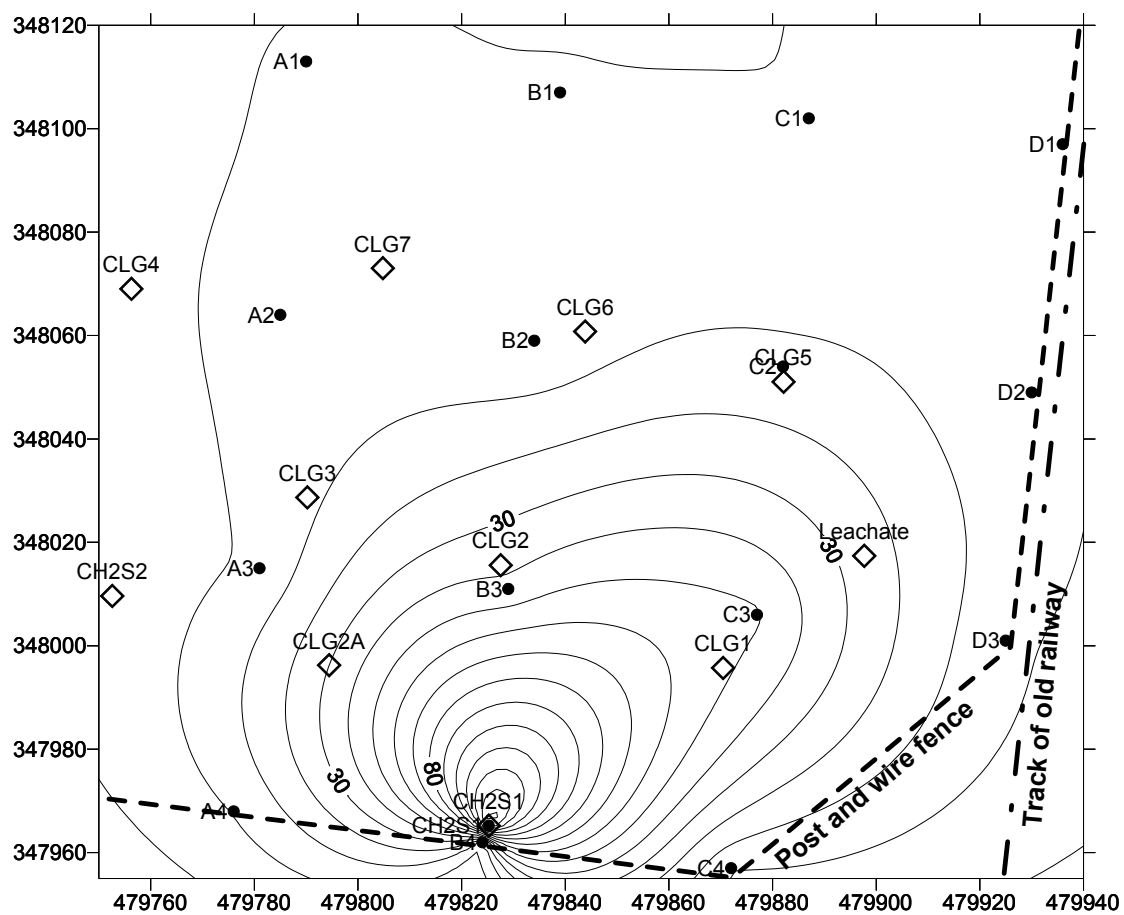


Figure 5.19. H_2S concentrations around vents on a landfill site. (Eastings and northings in metres. Concentrations in ppb H_2S .)

5.2 MEASUREMENTS OF PEAKS

5.2.1 Experiment A: Static HSPG measurements at Molehill Farm

The objective of this experiment was to assess the HSPG's response to H_2S in ambient air adjacent to a major road. The Molehill Farm site described in section 5.1 was used again to provide some consistency between the DR and HSPG monitoring sessions. With the wind in the prevailing direction, the HSPG was used to monitor the air at point 'Y' on Figure 5.1, for approximately one hour, and data recorded using the HSPG's built-in datalogger. During the monitoring, the HSPG auto-zero times were noted along with the times of any H_2S smells.

The results from this experiment are shown in Figure 5.20. The first 200 seconds are the 'settling period' after switching on. A manual zero was made at 300 seconds and auto-zeros occurred thereafter at approximately 500 second intervals.

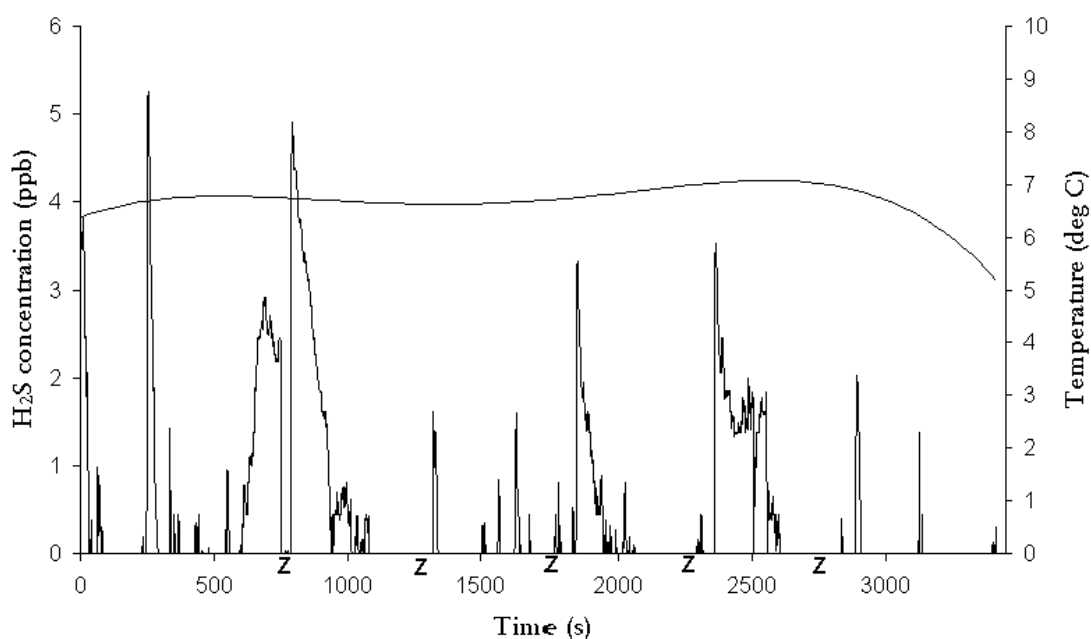


Figure 5.20. HSPG and temperature readings alongside the M1 motorway (Winter) showing a very rapidly changing H_2S concentration against an almost constant temperature. Zeroing periods marked as 'Z'.

5.2.2 Experiment B: Static HSPG measurements at Molehill Farm

This experiment was a repetition of that described in section 5.2.3 but at a different time of year. A separate temperature logger was used to monitor the ambient air temperature at the input to the HSPG. The results are shown in Figure 5.21. A manual zero was forced 420 seconds after switching on, and thereafter auto-zeros occurred approximately every 420 seconds.

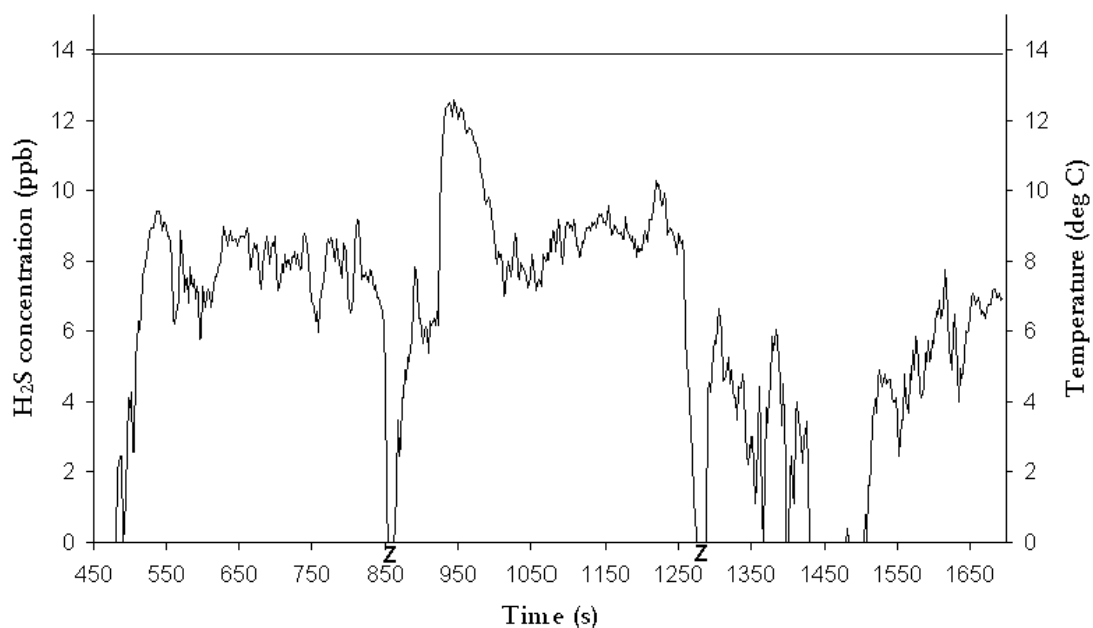


Figure 5.21. HSPG and temperature readings taken alongside M1 motorway (Early summer) showing a very rapidly changing H₂S concentration against an almost constant temperature. Zeroing periods marked as 'Z'.

5.2.3 Experiment C: Mobile HSPG measurements on a 40 mile road trip

Whereas the measurements described in sections 5.2.3 and 5.2.4 were static, this experiment was conducted using the HSPG on a motorway journey across the UK Midlands in the manner described in section 5.2.1. The results are shown in Figure 5.22. Events, and information about the environment through which the vehicle was passing, are detailed in table 5.1. The objective of the experiment was to compare the values of roadside H₂S concentration, obtained in the previous two experiments, with those concentrations which might be experienced by a driver on

a similar road.

Table 5.1.

Time	Event
0	Commencement of journey. Residential area.
330	Joined A5 dual carriageway
400	Auto-zero
630	Joined M42. Entered rural area.
860	Auto-zero
1430	Auto-zero
1500	Outskirts of Ashby-de-la-Zouch
1600	Manual zero
1630	Adjacent to Lount landfill site
1920	Auto-zero
2000	In cutting. Passed sewage works.
2290	Joined M1. H ₂ S smelt by vehicle occupants.
2380	Left motorway at Junction 24

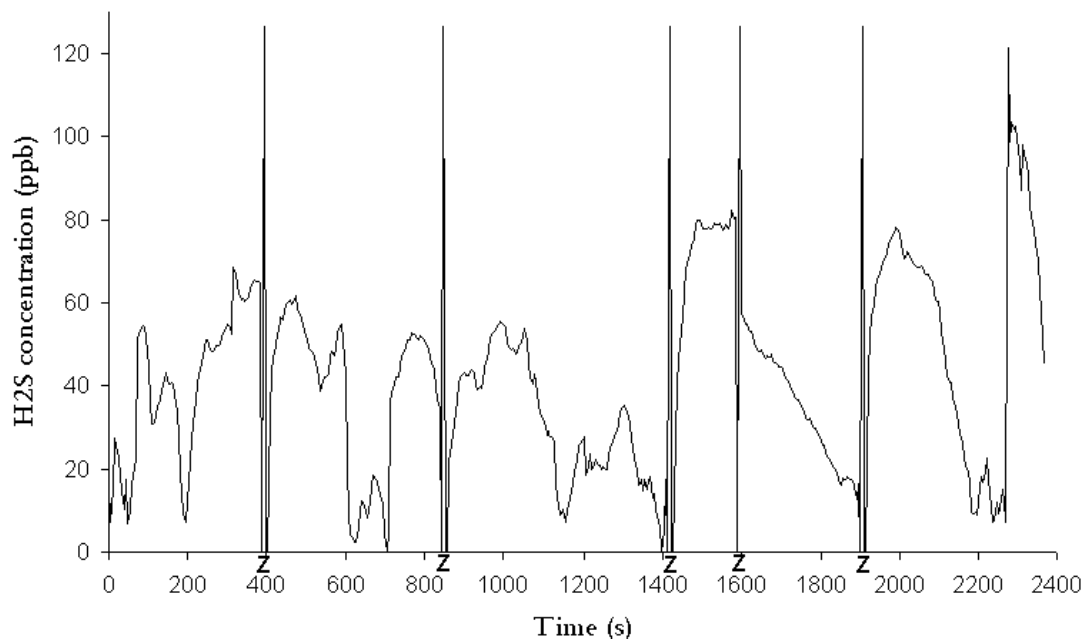


Figure 5.22. HSPG readings within a vehicle on a UK midlands road journey showing a very rapidly changing H₂S concentration. Zeroing periods marked as 'Z'.

5.2.4 Experiment D: HSPG measurements from a landfill site survey

This experiment was carried out on the same site as that described in section 5.1.12. The whole site was traversed, as described in section 5.1.14, and single readings taken at each grid intersection point. The objective was to make a simple comparison between the two measurement methods (DR and HSPG). The site was traversed in the order A7-A2, B2-B7, C7-C1, D1-D7, E7-E1, F1-F8 and G6-G1. The results are shown in Figure 5.23.

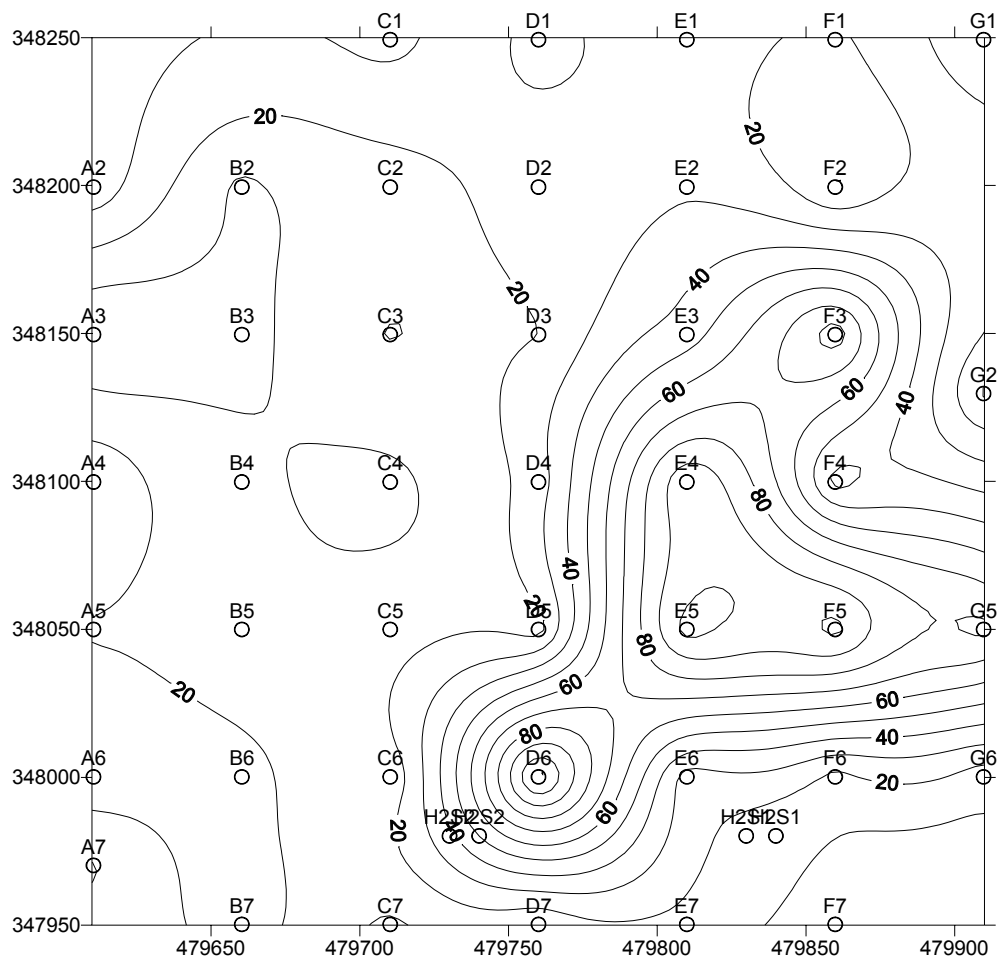


Figure 5.23. HSPG survey of whole landfill site. Contours show ppb H₂S. Eastings and northings in metres.

5.2.5 Experiment E: A detail survey of a landfill site using the HSPG

This experiment was also carried out on the south eastern quarter of the landfill site, and during the same period, as Experiment 15 described in section 5.1.15. The same portion of the site was traversed, in the same order, several times during the daytime on each monitoring day. These additional readings were used in this experiment in addition to the DRs to verify the two different approaches and obtain a simple comparison between the results during the same monitoring period.

The results for each traverse of the site are shown in Figures 5.24 to 5.33. A composite of the results obtained using the HSPG at each of the 16 locations is plotted in Figure 5.34. Contours show ppb H₂S. Eastings and northings in metres.

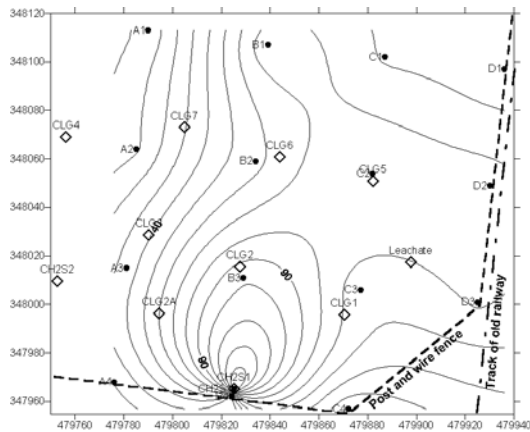


Figure 5.24. HSPG landfill survey.
Day 1, traverse 1.

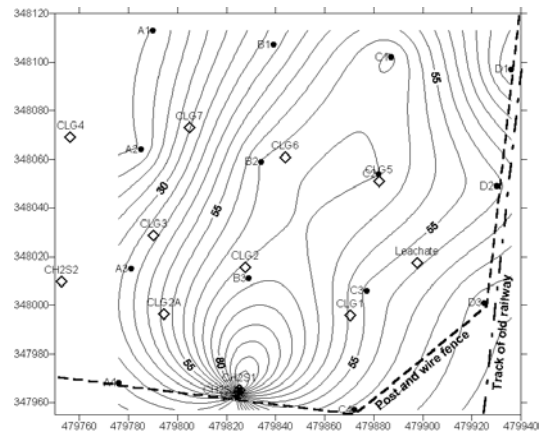


Figure 5.25. HSPG landfill survey.
Day 1, Traverse 2.

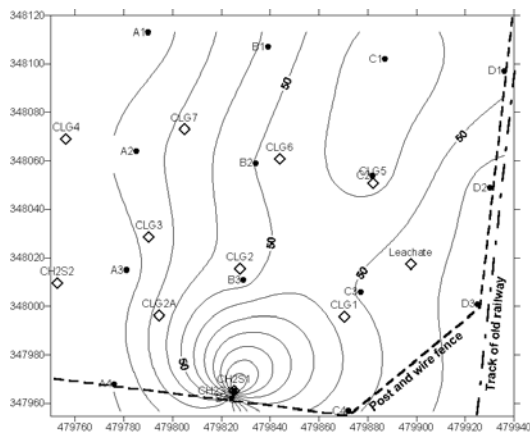


Figure 5.26 HSPG landfill survey.
Day 1, traverse 3.

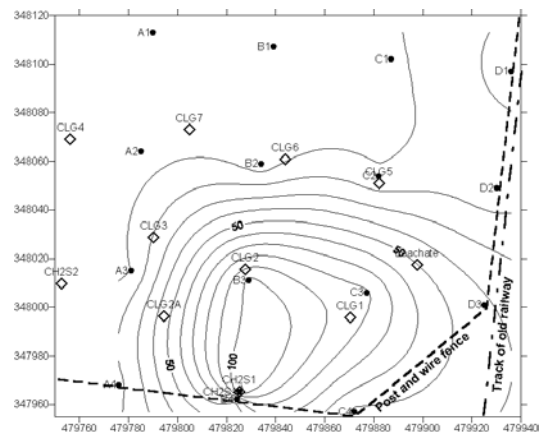


Figure 5.27. HSPG landfill survey.
Day 2, traverse 1.

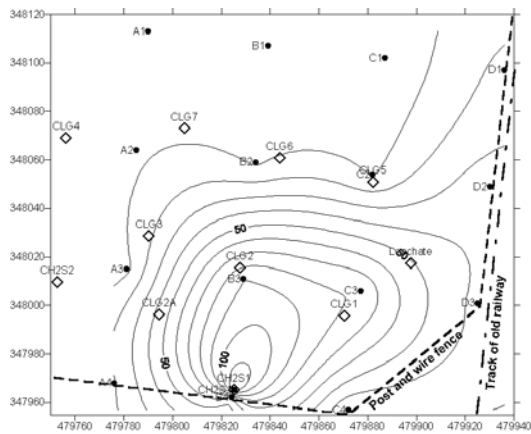


Figure 5.28. HSPG landfill survey.
Day 2, traverse 2.

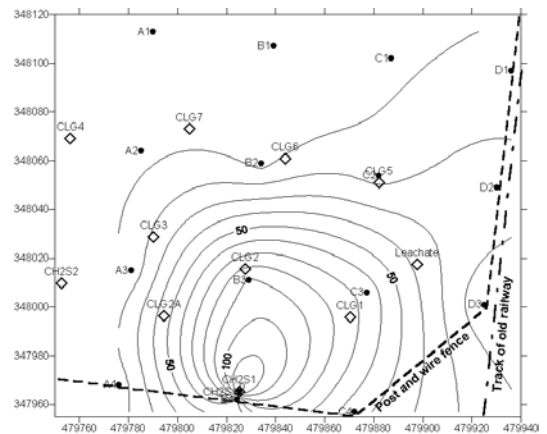


Figure 5.29. HSPG landfill survey.
Day 2, traverse 3.

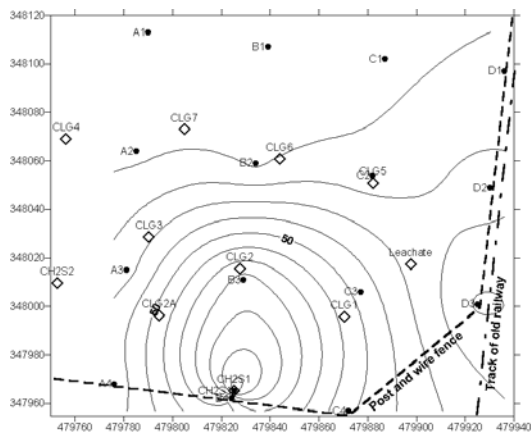


Figure 5.30. HSPG landfill survey.
Day 2, traverse 4.

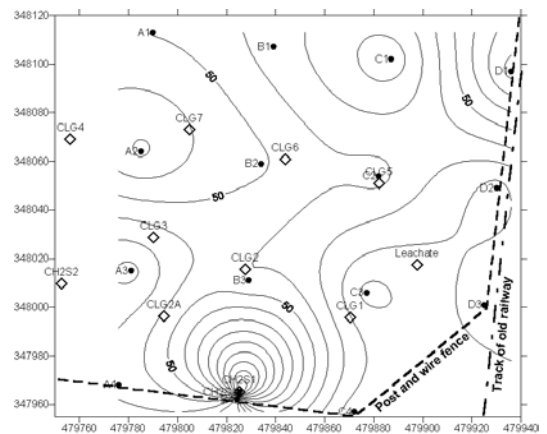


Figure 5.31. HSPG landfill survey.
Day 3, traverse 1.

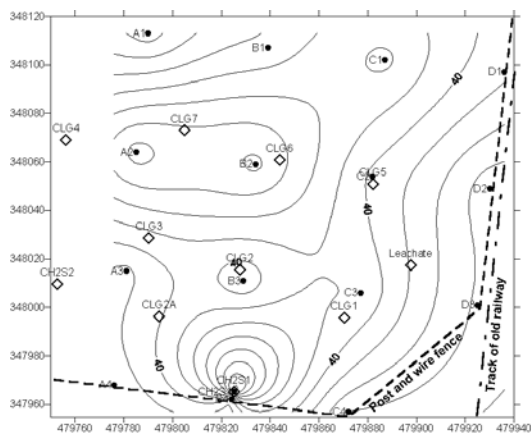


Figure 5.32. HSPG landfill survey.
Day 3, traverse 2.

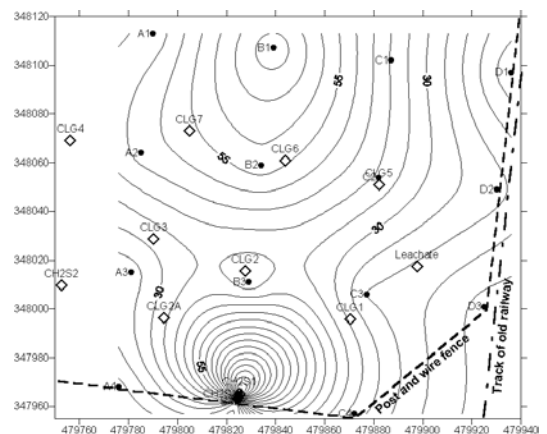


Figure 5.33. HSPG landfill survey.
Day 3, traverse 3.

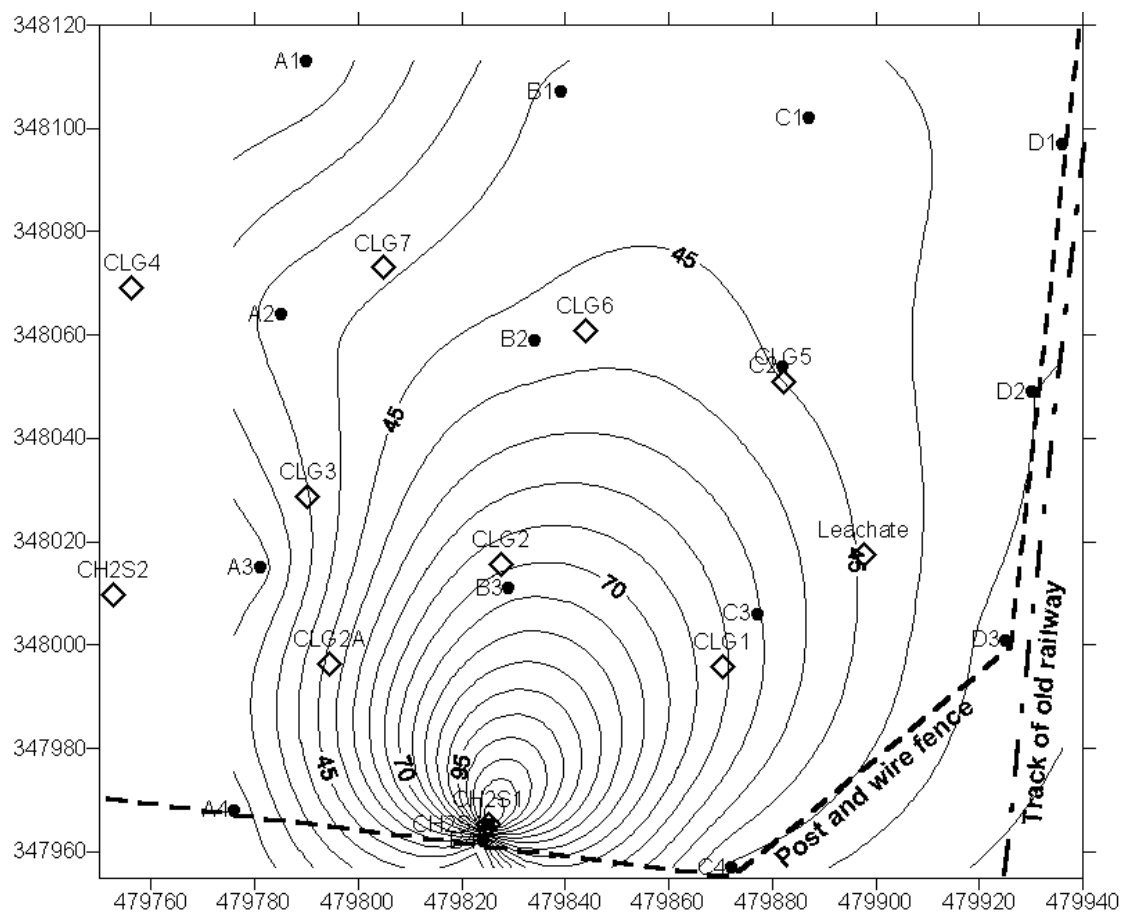


Figure 5.34. HSPG landfill survey. Composite of traverse results. Contours show ppb H_2S . Eastings and northings in metres.

Chapter 6: DISCUSSION AND CONCLUSIONS

6.1 LONG TERM MEASUREMENTS

6.1.1 Experiments using aspiration

These experiments (Experiments 1 - 4, section 5.1) used bubblers upwind and downwind of the M1 motorway at Molehill Farm to detect any elevation in H_2S concentration due to the road. The results of Experiments 1, 2 and 3 showed that the total amount of sulphide measured in the downwind dreschel bottles was higher than that in the upwind bottles. However, because sulphide was detected in the third of the three of the bottles at the downwind site, it was not appropriate to estimate an average H_2S concentration over the sampling period. This is because it was possible that not all the sulphide inspired had been captured by the solution in the bottles, and that some was exhausted back to the atmosphere. The differences in absorbance between the upwind and downwind sites, obtained in the three experiments, was not large (ie within $\pm 10\text{-}15\%$) and therefore it was possible that these differences might have been within experimental error, which was initially estimated as $\pm 10\%$.

Experiment 1 used bubblers with plain tube outlets whereas subsequent ACU experiments used bubblers fitted with perforated caps, as described in section 3.2, which improved H_2S capture. In Experiment 1 the absorbances obtained for the three bottles, in each ACU, were similar - within 20 % of each other. This result suggests that the total mass of sulphide entering the ACUs exceeded the capture capabilities of all three bottles at each location and therefore could account for the similarity in the two totals. Experimental errors were considered to see whether this experiment had any statistical significance in spite of this. Two possible sources of error were identified between the samples. The first possibility was in incorrectly making up the solutions to volume during analysis. This would be only a fraction of a per cent and was discounted. The second possible source of error

was in the readings obtained from the colorimeter, which was working at the lower limit of its range. If the readings recorded were analysed, with an error range of 1 digit, then a marginal significance ($p < 0.05$) was obtained for the differences in absorbance between the samples from the two locations.

In Experiment 2, each successive bottle in each ACU group captured slightly less sulphide than its predecessor. However the presence of sulphide in the third bottle of each ACU still indicated inadequate capture overall. A similar statistical approach to experimental errors, as that described in relation to Experiment 1, showed the results also had significance ($p < 0.05$).

Experiment 3 showed, for the first time, no sulphide capture in the third upwind bottle and very little in the second bottle. Although the exposure period was more than eight times longer than that of Experiment 2, the ambient H_2S concentration at the upwind site was lower than that previously measured. This concentration was therefore within the collection capability of the upwind ACU. However the presence of sulphide in the third downwind bottle again meant that any absolute comparison was of little value. The difference in the totals measured indicated a higher statistical significance ($p = 0.015$) than that of Experiments 1 and 2.

The other point of note in the results from the first three experiments, was that the sampling duration did not appear to be closely related to the absorbances obtained. This might, of course, have been a genuine variation in atmospheric H_2S concentration between the different sampling dates. However, it might also have been due to increased oxidation of the absorbed sulphide in solution, because of the longer sampling period, as discussed previously in Chapter 3. In particular, the absorbances obtained in Experiment 3 (section 5.1.3) were much lower than those obtained for Experiments 1 and 2 (sections 5.1.2 and 5.1.3) than would be expected for the longer sampling duration. This might have been because of changes in humidity (see Chapter 1)(Cadle and Allen, 1971), however, the general weather conditions on all these days were cool and damp and therefore

absorbances roughly correlated with exposure time might be expected.

Because of these apparent discrepancies, the objectives of these three experiments were not considered fully met but they did demonstrate the basic viability of the ACUs, the ability to capture sulphide in low ambient H₂S concentrations and that there was a statistical significance in the difference between the H₂S concentrations upwind and downwind of the motorway.

The ACU measurements made alongside the M1 motorway between junctions 23A and 24 in Experiment 4, which used the new absorbing solution described in section 3.2, showed that sulphide was not detected in either of the third bottles, from the upwind and downwind sites. From this it could be inferred that all the sulphide, in the volumes of ambient air sampled at each location, was captured by the solution in the first and second bottles. The work on the ageing of sulphide in solution, described in section 3.2.4, demonstrated that the sulphide captured did not oxidise appreciably during the sampling duration of 26 hours, and therefore that the mass of captured sulphide was indicative of H₂S concentration at each ACU location.

The results from Experiment 4, indicated a H₂S concentration of approximately 4 ppb (vol/vol) of hydrogen sulphide downwind, and 2 ppb upwind, of the motorway. A number of experiments were conducted with the wind in opposite directions at different times and in each case the upwind H₂S concentration was similar, and the downwind concentration was 1 - 2 ppb higher. This consistency implied that the extra contribution was not merely due to an unknown local source but was probably due to vehicles on the road. The ACU method was therefore considered validated for use in this context. The new absorbing solution was also shown to have an improved sulphide capture ability, over that previously used. The upwind H₂S concentration of approximately 2 ppb is consistent with that suggested by other workers for a rural environment (eg. Andersson *et al.*, 1974).

6.1.2 Experiments using DRs

Experiment 5 was the first occasion in which DRs were used in the field. Five sites were used as described in section 5.1.5. Although varying amounts of sulphide were captured at each site over the 24 hour duration, these variations were within $\pm 20\%$ of the mean value obtained. Therefore the variations might have been due to experimental error between the non-replicated DRs, and further investigation was deemed necessary to estimate the likely actual errors. However, the results obtained did suggest that there was an elevation in sulphide concentration downwind of the motorway at both LWE and J24E compared with the upwind and rural sites J24E and F12. These results therefore supported the findings previously obtained with the ACUs. There did not appear to be any more H_2S captured at the treatment works (KWT) than the upwind and rural locations. Some elevation of H_2S concentration was expected but it might be that the sulphide emissions were in other forms such as SO_2 or di-methyl sulphide (DMS).

For Experiment 6, only two sites were used with DRs, but three replicates were set out at each. One site was adjacent to a motorway (WG) and the other was a rural location (TL). The results showed that there was approximately 50 % more sulphide captured, and therefore a 50 % higher H_2S concentration, at the side of the motorway compared with the non-motorway location.

The variations between replicates in Experiment 6 were, however, greater than expected (coefficient of variance " 100 %). The highest sulphide concentration at the rural TL location exceeded the two lower values of the three replicates at the motorway adjacent WG location although the total sulphide captured was much higher at WG than TL . This finding brought the whole procedure into question and prompted a full review of the laboratory procedures before and after capture.

Experiment 7 used the DR method for a 10 day period at a single site and showed that at a rural, riverside location, the amount of hydrogen sulphide in the air was

low (between 1-2 ppb), which was in accordance with results from similar locations elsewhere. However, there was still a large variation between replicates apparent (coefficient of variance = 60 %). In this case it was considered that the manner in which the membranes on the DRs were initially treated on their return to the laboratory was crucial to the results obtained. The procedure which was finally adopted was fully described in section 3.2.5 and ensured that the membrane pores were fully cleared at the start of the analysis. All subsequent experiments showed much smaller standard errors ($SE \leq 0.14$).

Experiment 8, using DRs to make upwind and downwind comparisons of H_2S concentration alongside a major road and at a rural location, used three of the locations used in the first DR experiment (Experiment 5) but for three times the duration of the previous exposure. The locations were adjacent to a field on the University campus at Sutton Bonington (F12) and upwind and downwind of the M1 motorway at Long Whatton (LWW and LWE respectively). The results were compatible with those previously made, and the absorbances obtained for the replicates were very similar at F12 and identical at the other two locations. This was taken as confirmation of the importance of the procedure for membrane treatment during analysis.

Experiment 9 was a repeat of Experiment 8, but with a measurement period of one week, to see if the H_2S concentrations measured varied appreciably from the time of one experiment to another. The longer sampling duration of Experiment 9 was incidental, but a major change in the conditions between the two trials was that the wind direction changed approximately 180°. The results were compatible with those previously obtained and again the replicates showed similar concentrations ($SE \leq 0.14$). The rural F12, and motorway downwind and upwind, H_2S concentrations were also similar in both experiments.

Experiment 10 was to obtain simultaneous collection of data from five sites using DRs, so that direct comparisons in the H_2S concentrations at these locations could

be made over the same time period. There was reasonable agreement ($SE \leq 0.14$) between the replicates at each site. The rural F12 site and the upwind motorway site (LWW) showed similar concentrations of H_2S . Downwind of the motorway at LWE there was an elevation of H_2S concentration and a still higher elevation between the two major roads at MHFM. A similar elevation of H_2S concentration to that found at the MHFM site was found downwind of Kegworth water treatment works (KWT).

Experiment 11 provided similar results to Experiment 10 and the inclusion of MHFW gave an upwind and downwind comparison of H_2S concentrations on the A453 dual carriageway. The highest H_2S concentrations however were found upwind of the water treatment works KWT. This was surprising, but could be related to emissions from an animal house which lay upwind of KWT, or to emissions from the KWT outfall, which runs in a narrow open ditch to the north-east.

Experiments 12 to 15 showed that the DRs could be used for mapping H_2S contours around a known source. The data obtained also enabled the location of a previously unknown H_2S emission areas on this site for possible future remedial work by the site owners.

In Experiment 12 a cover box technique was tested as a means of measuring ground emissions of H_2S . It was later realised that the smell of H_2S at this point could be attributed to the plume of landfill gas being borne along the narrow valley from the valve CH2S1 to the cover box location. The H_2S concentrations obtained at the Adj, Mid and Vent DR posts (Figure 5.15) show how rapidly these concentrations diminished along a transect from a point source. These results were substantiated by those obtained in Experiments 13 to 15. The inference which may be drawn from these results is that H_2S in the atmosphere reacted with other chemicals to, or was diluted in the atmosphere by, approximately 90 % of the concentration at the emission source, in travelling a distance 140 m.

The use of un-replicated DRs in Experiments 13 and 14 was considered sufficient to reveal hot-spots of H_2S emission from the landfill site surface and from around valves in a reconnaissance survey. Preliminary mapping was then used to determine which area of the site was most appropriate for further detailed monitoring with replicated DRs. The results obtained confirmed the extremely rapid reduction in H_2S concentration with distance, from the known source discovered in Experiment 12, and described above. Experiments 13 and 14 showed that this rapid reduction occurred in all directions.

In the detail survey (Experiment 15), a very high concentration of H_2S was found around one particular vent but this concentration diminished to virtually zero, approximately 100 m away from the source. The H_2S concentration contours were very tightly packed between the vent CH2S1 and the post B4 (Figure 5.19). This irregularity was probably accentuated by the steep gradient, and consequent difference in elevation of about 3 m, between these two points. This is evident from the topographical map (Figure 5.18). Another contributing factor to the concentration gradient might have been that the gas emissions were at an elevated temperature, and also tend to jet vertically upwards from the leaking valve.

6.2 MEASUREMENTS OF PEAKS

The results of Experiment A (section 5.2.1) show the response of the HSPG in ambient air downwind of a major road and therefore indicate how the H_2S concentration fluctuates rapidly, and considerably, over time. The response is very similar in character to that found by Cadle and Mulawa (1978) in laboratory experiments into the production of H_2S resulting from vehicular catalytic converters. Characteristically there are small variations in low concentrations of H_2S which are interspersed with relatively large but brief transitions to concentrations several times larger in magnitude.

It should be noted that although some temperature variation was evident during the monitoring period, this bears no relationship to the HSPG readings. This confirms the assertion in Chapter 4, that the HSPG response is not temperature sensitive, but might also suggest the oxidation of ambient H_2S is not particularly sensitive to changes in temperature either. (This was also indicated by the experiments undertaken with the ACUs and DRs discussed in section 6.1.) However, the peaks of H_2S found were much smaller in amplitude than those resulting from Experiment B (section 5.2.2) which was conducted at a different, and warmer, time of year.

It is apparent that the character of the graphical data from experiment A is different to that from Experiment B. Experiment A shows a near zero baseline which is occasionally broken by the rapid fluctuations already described. Experiment B appears to show an elevated base line with more frequent excursions which are rather smaller than those of Experiment A. There is no reason to suspect instrumental changes, because the HSPG performed similarly in all laboratory calibrations, therefore an alternative explanation is needed for the differing behaviour.

It must be assumed that vehicles passing on the nearby roads were statistically

similar when considered as a group, both in vehicles passing per hour and in proportions of each vehicle type. It is also reasonable to assume that an equivalent number had catalytic converters which were operating under similar conditions. Higher humidity levels will cause a more rapid oxidation of H_2S to SO_2 because H_2S is highly soluble in water (see Chapter 1). Therefore, in minimal wind conditions, this reaction will occur more quickly before reaching the monitoring point. Higher wind speeds would reduce the transit time from source to the monitoring point, but would also result in greater mixing, and therefore dilution, of the H_2S . The most likely explanation however, is that, regardless of the precise mechanism, the results from Experiment B are actually showing a large number of peaks of H_2S concentrations, which are following each other in rapid succession, rather than an elevated base line with smaller peaks superimposed. The latter view would be in conflict with our original assumptions concerning vehicle numbers and type.

The results of Experiment C, conducted from within a moving vehicle, show H_2S concentrations two orders of magnitude higher than Experiments A and B. This is consistent with the work of Clifford *et al.* (1997) who also found that concentrations of certain vehicular pollutants (which did not include H_2S) were several times higher within vehicles travelling along a road than those measured at the roadside. Both studies therefore indicate that the results from contemporary roadside pollution monitoring sites, put in place by governmental and other bodies, must be considered in context. Results from roadside sites might be safely used in a consideration of the effects of vehicle pollution on people and property adjacent to the road, but would seem to be appreciable underestimates of the effects on road users.

The HSPG was designed to monitor intermittent peaks of H_2S against a low background value, but in Experiment D the instrument was used to measure relatively constant concentrations at a series of fixed locations on a landfill site. Although this was not a direct comparison with any of the measurements taken

using DRs, the HSPG results show a similar pattern of concentration to that revealed by the DR method on other occasions. This suggested that either monitoring technique could be used for a similar purpose of site mapping, within certain constraints.

Experiment E was designed to obtain a qualitative comparison of results from the HSPG and DR methods. Both methods show the same hot-spots in similar concentrations. Direct comparison of the results obtained using the DRs and the HSPG is not strictly valid because both sets of instrumentation were not deployed continuously throughout the monitoring period. It would not be sensible to compare a single HSPG traverse of the whole site with the results from the DRs which were exposed for the whole 50 hour period. However, the results obtained using the two methods are qualitatively in agreement when the DR results are compared with the average of the HSPG results.

6.3 CONCLUSIONS

The catalytic converter is a reaction chamber for numerous catalytic and conventional reactions between compounds which may contain impurities. It is therefore not surprising that the production of hydrogen sulphide was discovered accidentally rather than predicted theoretically.

Roadside and ambient measurements of hydrogen sulphide have been made. The results show a small but repeatable elevation of mean H_2S concentrations downwind from a main road. The ambient rural H_2S concentration was consistently measured as 1-2 ppb. Busy main roads appear to add approximately 1-2 ppb H_2S to the mean ambient value when measured at the roadside. Therefore, in relation to the first objective stated in section 1.3, it is now clear that this additional pollution load is probably not significant in either local or global terms. The second objective, to measure atmospheric concentrations of H_2S , is also met, and the H_2S concentrations measured agree with those of other workers.

For drivers and passengers in vehicles on busy roads however, the situation is rather different. Drivers, and passengers, on such roads are subjected to a series of relatively high peaks of concentration of H_2S gas, whose amplitude may be measured in 100's of ppb. The third objective, stated in section 1.3, was to investigate the relationship between peak and long term concentrations of H_2S and this work suggests that, in a road side or on-road environment, it would appear that it is the integration of these brief peaks that is the cause of the elevation of mean ambient H_2S downwind of the carriageway. This is a new area of research and the field measurements obtained as part of this study confirm the theoretical expectations and also measurements made previously in the laboratory by others.

Whilst, as discussed in Chapter 2, a considerable amount of work has been done worldwide on the human health effects of H_2S at low ambient concentrations, as a result of industrial pollution, and at very high, life threatening, concentrations,

as a result of industrial accidents, there appears to have been no research directed at assessing any effects on human physiology which might be due to vehicular pollution in the manner found in this study.

Alternative measurement methods have been identified, both for passive background measurement and also for short term, rapid response measurements. The latter included the development of a new resistance sensor and its incorporation in a new piece of equipment for use in the measurement of low concentrations of H_2S gas. This required the specialist development of conventional analogue electronic techniques.

The Diffusion Reservoirs provide a reliable, low cost, method of measuring average H_2S concentrations. The method produces results which are in agreement with those obtained by other means. The results indicated the additional ambient H_2S pollution, due to catalytic converters fitted to road vehicles, and also clearly revealed the 'hotspots' of H_2S concentration on a landfill site. The hotspots were associated with failed valves in the gas extraction system and with sub-surface fissures in the land fill cover. The results also indicate that the concentrations of H_2S at the perimeter of the site are of relatively minor significance.

The HSPG enabled the detection of transient peaks of H_2S for the first time in a portable instrument and completed the fourth objective stated in section 1.3. There is, however, considerable scope for further improvements to this prototype. Fine tuning of the electronics, such as determining the optimum component values for the differentiator for a particular input range, would be a relatively minor issue, but it is believed that considerable improvement could be made to the instrument by making a number of modifications to the sensor cell. These might include:-

- 7 improved cell geometry to minimise 'dead' space above the sensor surface. The present 9 mm above the sensor surface could be reduced to 1 or 2 mm which should reduce the response time approximately in proportion.

- 7 changes in the size of the sensor and/or alter the spacing of the electrode 'fingers' and their fineness. With combination of these approaches, it should be possible to increase the effective 'length' of the electrodes within a smaller area and thereby increase not only the sensitivity of the device but also further reduce the response time. Gold plating of the copper electrodes should also minimise corrosion and increase the re-usability of the sensor.
- 7 improved containment of both sets of carbon granules and refinement in the size of granules. Finer granules mean that airspaces between them are minimised and also increases the unit area for adsorption of H_2S onto a given volume of carbon due to the 'scale effect'. Shortening of the gas flow path, whilst ensuring the absorption of the maximum H_2S , is particularly desirable. This will minimise the opportunity for mixing, dilution and reaction of the H_2S and yield potentially more accurate results with a more rapid response time.
- 7 the use of a non-gel surface coating - such as tungsten trioxide - to improve stability and also to reduce the re-coating frequency. Gold electrodes could be sputtered directly onto the sensor surface or applied using a chemical deposition technique.
- 7 The variation in sensitivity over time with the gel sensor only occurs within a narrow band and so the millivolt display could be conditioned to read ± 10 % ppb directly for field use. This would be particularly appropriate if the gel coated sensor is replaced by a metallic oxide sensor as described above.
- 7 The possible sigmoidal response of the gel sensor warrants further investigation if the gel coating is developed further. This would require a calibrator of suitable output range to locate the possible upper end of the

curve where increasing H_2S concentration resulted in proportional less voltage change.

Some of the results obtained led to suggestions that ambient H_2S concentrations may be affected by meteorological conditions. It is suspected that ambient concentrations monitored will be subject to seasonal variations, which are due to changes in the reactivity of H_2S and other chemical compounds. This would require further investigation, but temperature and humidity are indicated as factors. It is also suspected that atmospheric pressure will affect the emission rate for gases originating from landfill sites.

Appendix A:

MEASUREMENTS FROM COMMERCIAL INSTRUMENTS

7100 H₂S Analyser

A borrowed model 7100 H₂S bench analyser (MDA Scientific) was used on a number of occasions to measure H₂S alongside major roads. This mains operated piece of equipment was used outside in conjunction with a portable generator placed downwind. The analyser was operated in its 'continuous' mode which prompted it to measure ambient H₂S concentration as frequently as possible. On average this resulted in a reading being taken at least every 30 seconds.

The readings obtained using this equipment suggested that peak roadside H₂S concentrations, due to vehicle emissions, reached 100 ppb.

Single Point Monitor (SPM)

A borrowed SPM instrument (MDA Scientific), fitted with an H₂S Chemcassette was also used on a number of occasions to measure H₂S alongside major roads. Like the model 7100 analyser, this gave readings approaching 100 ppb. However, it was noted that approximately 15 minutes after switching on the instrument, that the readings always diminished in magnitude.

Discussions with the manufacturer came to the conclusion that the impregnated paper tape used in this instrument was becoming bleached during measurement by SO₂ and readings were discontinued. The results obtained did, however, confirm the magnitude of those readings of H₂S concentration obtained with the 7100 toxic gas analyser.

Jerome 631X portable H₂S monitor

A Jerome 631X H₂S monitor (Arizona Instrument Corporation) was borrowed from Able Instruments and Controls Ltd and used, in conjunction with an early incarnation of the HSPG (see section 4.3.2), to monitor H₂S concentrations from within a vehicle whilst travelling on a major road.

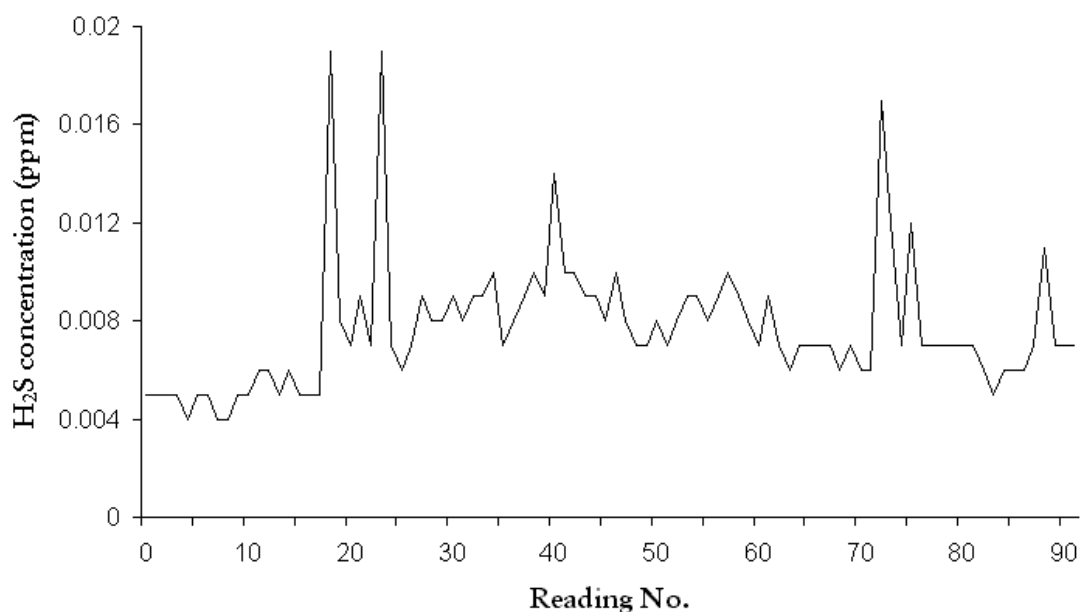


Figure A1 Output from Jerome 631X taken during a trip on a major road

The results from the Jerome 631X are shown in Figure A1. The readings from this instrument show peaks of H₂S concentration much lower than those obtained using the MDA Scientific instrumentation. This is believed to be because of differences in the way the sample is analysed within the instruments, as discussed in section 4.1, and that the Jerome 631X missed the actual concentration peaks.

Appendix B: HSPG DIFFERENTIATOR ANALOGY

The action of the HSPG differentiator (Chapter 4) may be explained by a mechanical analogy.

Consider a smooth walled vertical tube in which there is a loose fitting cylindrical piston. The inside walls of the tube are coated with viscous lubricant such that the piston tends to slide slowly downwards due to gravity, but if the tube is moved up or down steadily at a velocity greater than the sliding speed of the piston, then the piston will tend to follow the imposed motion. Conversely, if the tube is moved too rapidly then the inertia of the piston will tend to keep it in one place.

The vertical motion of the tube is analogous to the differentiator input voltage and the motion of the piston is analogous to the output voltage. The viscosity of the lubricant is a measure of the capacitance in the input stage. Very rapid movements of the tube are analogous to electrical noise which will be integrated by the capacitor (lubricant). Slow variations in sensor output, due to drift, will be masked

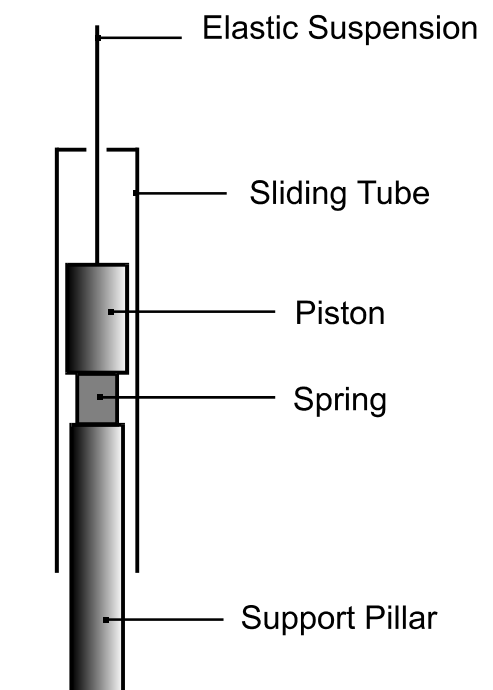


Figure 9.1. Mechanical analogy of the differentiator action

by the tendency of the piston to reach equilibrium (ie the limit of downward movement). Between these two extremes, moderately fast movements of the tube will be followed accurately by the piston - over short time scales. The dynamics of system depend solely on the lubricant's viscosity.

To continue the analogy, the piston is freely suspended by a long elastic cord through a cap at the top of the tube and, with no movement of the tube (ie. zero change in input), will reach equilibrium at a point where the piston is barely touching the upper end of a fully expanded compression spring. The latter is, in turn, supported on a vertical pillar which fits easily within the tube (Figure 9.1).

Now, an upward movement of the tube will tend to carry the piston upward as before, but the higher they are raised (ie. the larger the input and output voltages), the greater will be the tendency for the piston to return to its equilibrium position. Not only will it still be under the influence of gravity, but it will also lose some support from the elastic (ie. capacitor leakage). Alternatively, downward movements from equilibrium will be assisted by gravity but opposed by the elastic and the spring (ie. diode forward current). The upper limit, on piston movement, is imposed by the tube cap (ie. the operating voltage of the circuitry, approximately +5 volts relative to the differentiator 5 V bias voltage, 0 V⁵), and the downward limit by the post supporting the spring (ie. combined in the form of the OA47 diode in the circuit diagram, approximately -0.3 volts relative to the 5 V bias voltage, 0 V⁵).

If the 'input' tube is raised and held at a new value (ie. a step change), the piston will initially rise by an equivalent amount. If there is no further movement of the tube then the piston will gradually slide down to its equilibrium position. This will be a decelerating, exponential fall however, as the piston will gradually experience the increasing tension in the elastic. This is analogous to the decaying voltage on the differentiator capacitor. Instead of a rise, if the input tube were to descend from the equilibrium position, then again the piston would fall, but would

experience not only increasing tension in the elastic, but also the upward force of the spring, and ultimately the support pillar. The exponential decay voltage on the capacitor is analogous to the elastic tension as before, and that of the spring is similar to the change in forward conduction current, with increasing voltage, of the germanium diode up to its nominal maximum forward voltage of 0.3 volts - which is represented by the downward limit to movement imposed by the support pillar.

Thus, if an initial upward step change is followed a short time later by a downward one of identical magnitude then the input tube will return to its start position. The output piston however will not because, during the interval between rise and fall, it will have slid a short distance downwards. Initially therefore the piston will descend to a point slightly below its starting position before returning to equilibrium in the manner described above. There is, however, no such thing as a 'negative' concentration of H_2S . So, provided that drift and noise are within the designed limits of the differentiator, then negative excursions of the piston (ie output voltage) will normally be due to this slippage. This corresponds to capacitor leakage, and results in what is commonly known as voltage 'droop' on the output of the differentiator.

Nevertheless, in spite of the in-built tendency toward equilibrium, it can be seen that over time, with successive and irregular changes in position of the tube, that the piston might gradually approach either the upper limit of the cap or the lower limit of the pillar - even if the sum total of all the input movements is zero. This would be due to the accumulated errors engendered by piston slippages - the analogy for capacitor leakages and diode conduction. Therefore, in 'auto' mode, every ten minutes the actual HSPG is switched to H_2S free air, the voltage at the differentiator input may be adjusted as previously described and the circuitry output can be manually zeroed. In the analogy, this is returning the tube to its 'start' position, and the piston to its equilibrium position, respectively.

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